Dynamical Threshold of Diluteness of Soft Colloids

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S *Supporting Information*

ABSTRACT: Soft colloids are hybrids between linear polymers and hard colloids. Their solutions exhibit rich phase phenomenon due to their unique microstructure. In scaling theories, a geometrically defined overlap concentration c^* is used to identify the concentration regimes of their solutions characterized with distinct conformational properties. Previous experiments showed that the average size of soft colloids remains invariant below c^* and varies characteristically above it. This observation reveals the causality between the conformational evolution and the physical overlap between neighboring particles. Using neutron scattering, we demonstrate that the competition between the interparticle translational diffusion and intraparticle internal dynamics leads to significant conformational evolution below c^*. Substantial structural dehydration and slowing-down of internal dynamics are both observed before physical overlap develops. Well below c^*, a new threshold of diluteness c_D^* emerges as the crossover between the characteristic times associated with these two relaxation processes. Below this dynamically defined c_D^*, the two relaxation processes are essentially uncoupled, and therefore, the majority of the soft colloids retain their unperturbed conformational dimensions. Our observation demonstrates the importance of incorporating dynamical degrees of freedom in defining the threshold of diluteness for this important class of soft matter.
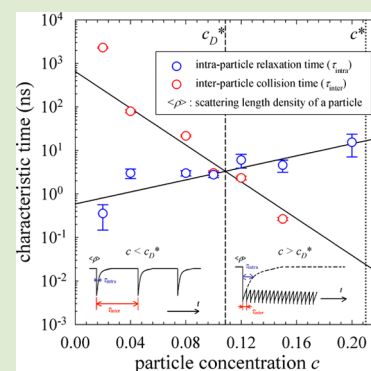
Soft colloids, such as star polymers, dendrimers, microgels, and some polymer-grafted nanoparticles, are synthetic macromolecules consisting of polymer branches emanating from the center of molecules. They have attracted considerable attention in part because of their intriguing globular but solvent-accessible colloidal architecture.[1−4] The interest in these systems increased even further because of numerous technological applications owing to the fact that they possess useful features of both polymers and colloids.[5] Consequently, they have been studied extensively in the last few decades.

One key feature that differentiates soft colloids from hard sphere or other densely packed particles is the flexibility of their molecular structure.[1−4] Understanding how this additional softness affects their conformation, interparticle interaction and phase behaviors have been the focus of extensive structural studies of soft colloids.[1−4]

Similar to the scaling theories of linear polymers,[6] based on the physical size of an unperturbed soft colloid, an overlap concentration c^* is defined to categorize characteristic concentration regimes with distinct conformational properties.[7] Below c^* existing experimental results show that the size of soft colloids, in terms of radius gyration R_G, remains unchanged.[8] Since R_G is one of the most important conformational

parameters, this observation leads to an apparent recognition that within this dilute regime of $c < c^*$, soft colloids retain their unperturbed geometrical dimensions.

However, this structural softness also renders an additional degree of freedom to the dynamics of soft colloids in solutions. In addition to the center-of-mass diffusion,[9] many experiments have demonstrated that the dynamics of soft colloids in solution is characterized by intraparticle collective motions as well.[10] Whereas interparticle overlap does not occur below c^*, it can be envisioned that a coupling between these two characteristic dynamical processes can be introduced by the thermally driven interparticle collisions Thus, an important aspect about the definition of diluteness remains open: Whether within the geometrically defined dilute region of $c < c^*$ the dynamical coupling affects the single particle conformation and internal dynamics is not intuitively obvious.

We address this question through a neutron scattering study of poly(amido amine) (PAMAM) dendrimers, a model soft

colloidal system.[3] Aqueous solutions of two PAMAM dendrimers, generation 4 and 6 (G4 and G6) with different conformational softness, are studied in this report. We investigate the interplay between their interparticle diffusive and intraparticle internal dynamics when $c < c^*$. Contrary to general expectations that conformation and internal dynamics should be unaffected until c^* is surpassed, we demonstrate that the interplay between these two dynamical degrees of freedom produces a characteristic concentration dependence of the conformation and internal dynamics even at concentrations well below c^*. Moreover, the crossover of the characteristic relaxation times associated with these two relaxation processes gives rise to a new dynamically defined threshold of diluteness, below which the interparticle collisions play a minimal role in affecting the particle conformation.

The conformation of a dendrimer was shown to be closely related to the invasive water.[11] Therefore, it is instructive to begin the microscopic description of dendrimer with the consideration of the interpenetrating water. By including the coherent scattering contribution from the water, we extract the concentration dependence of dendrimer conformation below c^* using small angle neutron scattering (SANS) spectrometers available at D22, Institut Laue-Langevin, and at BL6, Spallation Neutron Source. The total scattering power of a single dendrimer, which we denote as $P(0)$, is a function of bound scattering lengths of the constituent atoms of polymer, the average scattering length density (SLD) of water, the packing density of invasive water and the volume of the intradendrimer cavities. By analyzing $P(0)$ (see Supporting Information (SI)), one can evaluate the conformational evolution of dendrimer from the variation of a single dendrimer SLD, $\langle \rho \rangle$, which takes the following expression

$$\langle \rho \rangle = \frac{b_{polymer}}{v_{polymer} + (1 - v_{water} \cdot h) \cdot v_{cavity}} \quad (1)$$

$b_{polymer}$ and $v_{polymer}$ in the right-hand side (RHS) of eq 1 are the sum of the bound scattering lengths and the volume of the constituent atoms of the polymer components of dendrimer, respectively, h is the number density of invasive water molecules, v_{water} is the molecular volume of water in its bulk state, and v_{cavity} is the total volume of the intramolecular cavities. It is worthy of note that, $v_{polymer}$, the volume of each molecule is determined by the atomic volumes and the bond lengths of the constituent atoms of the molecule, which are both independent of the concentration. It is different from the concept of partial molar volume, which takes into account the interactions between the solute and the solvent molecules and hence is concentration-dependent. We show $\langle \rho \rangle$ for G4 and G6 PAMAM dendrimer solutions studied in this work in Figure 1.

Similar to previous observations,[8] the radius of gyration (R_G) remains essentially unchanged within the concentration range of $c < c^*$. However, over the same concentration range $\langle \rho \rangle$ for both dendrimer solutions is a decreasing function of c. While explicitly separating the individual contribution of each physical quantity in the RHS of eq 1 to the evolution of $\langle \rho \rangle$ is not possible with our current methodology, a qualitative picture of the conformational evolution below c^* can certainly be deduced from the following argument. Provided that both $b_{polymer}$ and $v_{polymer}$ do not exhibit dependence on c, the decreasing trend of $\langle \rho \rangle$ in Figure 1 suggests that the magnitude of $(1 - v_{water} \times h) \times v_{cavity}$ must increase upon increasing c. Meanwhile, since the excluded volume effect can only cause a
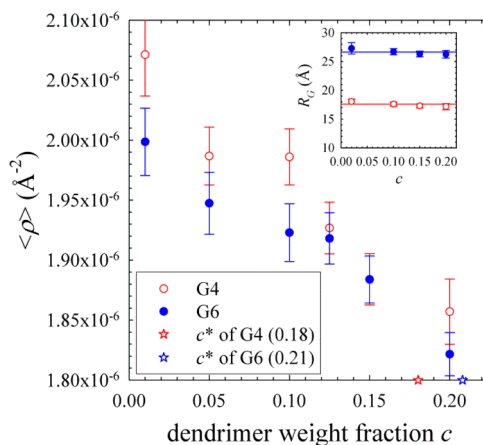

Figure 1. Average SLD of a single dendrimer $\langle \rho \rangle$ for G4 and G6 PAMAM dendrimer as a function of dendrimer weight fraction c in solutions. Evolution of R_G as a function of c is given in the inset.

contraction of intramolecular voids, it is clear that v_{cavity} is not an increasing function of c. As a result, h, the parameter quantifying the packing of invasive water, must decrease to ensure $(1 - v_{water} \times h) \times v_{cavity}$ is an increasing function of c. Therefore, steady dehydration of a single dendrimer caused by the increase in c well below c^* can be concluded unambiguously. It is instructive to compare the observed evolution of $\langle \rho \rangle$ with c with existing results of a conformational study of soft colloids below c^*. A static conformational picture of the soft colloid below c^* has been proposed based on the invariance of radius of gyration (R_G) observed by scattering experiments.[8] According to its mathematical definition,[12] R_G reflects only the integrated, thus, coarse-grained, information on the intraparticle density profile. It is therefore possible that in this system the detailed internal structural variation presented here is smeared out during the integration process and therefore may not be explicitly reflected in R_G.

As well as the $\langle \rho \rangle$ discussed above, the intermolecular structure factors of PAMAM dendrimer immersed in water with concentrations below c^* also demonstrates a steady and clear evolution, which implies that the structure may not be invariant even before the establishment of physical overlapping. With a whole series of concentrations, the $S(Q)$s of the G6 PAMAM dendrimer with the weight percentages of 4%, 8, 10, and 12% are given in Figure 2. It is noticed that the intermolecular structure factor $S(Q)$ starts to show a pronouncing interaction peak before reaching c^* ($\sim$20 wt %), which evidence the interdendrimer structural evolution in this low concentration regime.

To further explore the observed conformational variation below c^*, we investigated the interplay between the interdendrimer center-of-mass diffusion and intradendrimer collective motion using the neutron spin echo (NSE) spectrometer available at IN 15, Institut Laue-Langevin, and at NG5, NIST Center for Neutron Research. One distinct advantage of NSE is its ability to access wide spatial and temporal ranges of dynamics. This unique feature allows simultaneous determination of both types of dynamical processes for dendrimer solutions. Based on the procedures given in the Supporting Information, from the measured intermediate scattering functions $F(Q, \tau)$, the collective diffusion coefficients $D_S^{exp}(Q)$ of G4 and G6 PAMAM dendrimers are extracted and given in Figure 3.

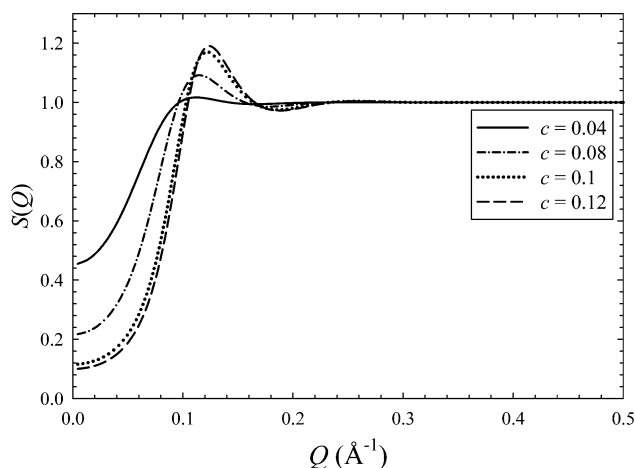**Figure 2.** Evolution of the intermolecular structure factor of G6 PAMAM dendrimer at different weight percentage c below c^* (solid, 4% in weight; dash-dot, 8%; dot, 10%; dash, 12%).
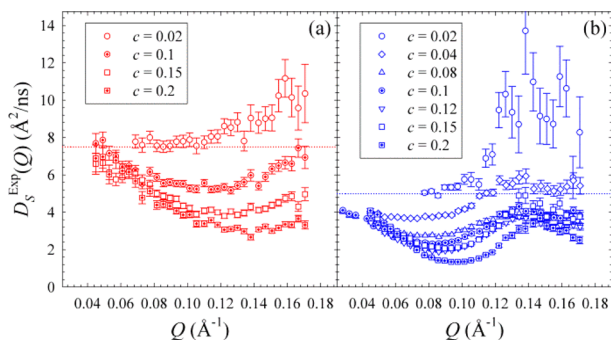

Figure 3. Collective diffusion coefficient $D_S^{exp}(Q)$ of (a) G4 and (b) G6 PAMAM dendrimers as a function of concentration. The dotted lines are the translational self-diffusion coefficients of G4 and G6 PAMAM dendrimers in aqueous solution with $c = 0.02$.

For a dilute concentration of $c = 0.02$, the contribution from the interdendrimer interaction can be disregarded. As shown in Figure 3, at low Q, the data agrees with the corresponding translational self-diffusion coefficients (dotted lines) given by the dotted lines. But significant increases in $D_S^{exp}(Q)$ are observed in the Q range of $Q > 0.12$ Å^{-1} for G4 and $Q > 0.10$ Å^{-1} for G6. Our SANS studies have demonstrated that the intradendrimer structural characteristics are indeed reflected within these Q ranges.[13] Previous studies of other dendrimer systems have identified the intramolecular collective motion as the origin of this dynamical enhancement.[10f,g]

Since the size of soft colloids shows no discernible dependence on concentration when $c < c^*$, as shown in the inset of Figure 1, it is reasonable to assume that all the information on intradendrimer dynamics is still contained within the Q range above 0.10 Å^{-1}. Indeed, upon increasing c to c^*, similar variations of $D_S^{exp}(Q)$ are observed in the Q region relevant to the internal motion. But changes occur also in the lower Q region relevant to larger interparticle length scales, indicating that the measured $D_S^{exp}(Q)$ contains contributions from both inter- and intradendrimer collective motions. Also, within this concentration range a steady establishment of interdendrimer interaction is revealed by SANS experiment (see SI). Therefore, the suppression of $D_S^{exp}(Q)$ in the whole Q range probed is caused by the increasing interdendrimer interaction as well as the hydrodynamic interaction.[14]

One way to quantify the interplay between the inter- and intradendrimer dynamics is via the comparison of their characteristic times. Based on an approximation inspired by analysis of protein dynamics in solutions (see SI),[15] the intradendrimer internal motion can be identified separately from the measured $D_S^{exp}(Q)$ via compartmentalizing the interdendrimer contribution. Namely,

$$D_S^{exp}(Q) \cdot Q^2 = D_S^C(Q) \cdot Q^2 + \Gamma_{intra}(Q) \qquad (2)$$

where $D_S^C(Q)$ represent the contribution from the interdendrimer collective dynamics and $\Gamma_{intra}(Q)$ is the Q-dependent frequency of the intradendrimer collective motion. Accordingly, we define the characteristic time for interdendrimer motion τ_{inter} as the average collision time between a tagged caged dendrimer and its surrounding neighbors. τ_{inter} can be determined from the short-time self-diffusion coefficient D_S^S, the average interdendrimer distance $\langle L \rangle$ and the size of dendrimer. In addition, after subtracting the contribution from the hydrodynamic interaction, the characteristic time for internal relaxation τ_{intra} can be obtained from $D_S^{exp}(Q)$ within the Q range of $Q > 0.12$ Å^{-1} for G4 and $Q > 0.10$ Å^{-1} for G6. The results of τ_{inter} and τ_{intra} as a function of c are given in Figure 4.
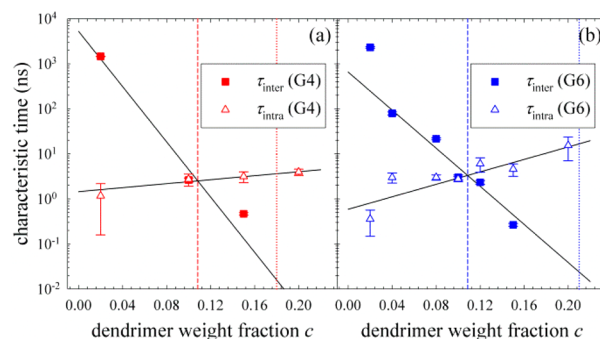

Figure 4. Average interdendrimer collision time τ_{inter} (filled circles) and internal relaxation time τ_{intra} (open circles) for (a) G4 and (b) G6 PAMAM dendrimers in water as a function of concentration c. The dotted and dashed lines respectively give the concentrations of c^* and c_D^* of G4 and G6 PAMAM dendrimers. Assuming both τ_{inter} and τ_{intra} evolve exponentially with c, c_D^* can be defined by the intersection of two solid lines, c_D^* is defined by the intersection of two solid lines.

Upon increasing c, τ_{inter} is seen to decrease by several orders of magnitude for both G4 and G6 dendrimers. This observation is a reflection of slowing down of the dendrimer self-motion, characterized by D_S^S, and a significant decrease in $\langle L \rangle$, caused by the increase in concentration. Meanwhile, with the influence of the hydrodynamic interaction, the minima of $D_S^{exp}(Q)$ provides the lower limit of the dendrimer self-motion and the maxima provides the upper limit of the total dynamics including the internal motion. Therefore, the difference between these two extremes gives the upper limit for the frequency of internal relaxation. Results of this qualitative estimation indicate a discernible increase of τ_{intra} upon increasing c below c^*. A quantitative analysis demonstrated in the SI suggests the increase in dendrimer concentration from $c = 0.02$ to 0.2 renders an increase in τ_{intra} by a factor of 4 and 40 for both G4 and G6 dendrimers. Although whether the NSE-measured internal collective motion of dendrimer is due to shape fluctuation or internal density fluctuation remains a subject of ongoing scientific discussion,[10a] the increase in τ_{intra}

below c^* clearly indicates that this internal dynamics are progressively restricted and decelerated by the increase in the frequency of physical contact with its neighbors due to the concentration effect. From the SANS data analysis presented in SI, it is reasonable to assume that the equilibrium conformations of both G4 and G6 dendrimers at $c = 0.02$ are free from the influence of interdendrimer interaction. The increasing τ_{intra} indicates that even below c^* dendrimers are indeed restrained from fully relaxing to their original conformation at $c = 0.02$ due to the progressively shortened dendrimer−dendrimer collision time interval. Here the lowest concentration of $c = 0.02$ is considered dilute solution in both the measurements of SANS and NSE. Note that the effective volume fraction given in Table S1 of SI is not the actual volume fraction occupied by the polymeric molecules. Besides, due to the different potential forms of soft colloid interaction from hard colloids, at the same volume fraction, the features from the interactions shown in the structure factor of a soft colloid solution is much less pronounced than that of hard colloidal solution.[16] Therefore, we surmise that the variation of intradendrimer hydration is a structural manifestation of the interplay between inter- and intradendrimer dynamics influenced by the concentration effect.

It is worth noting the correlation between the evolution of τ_{intra} presented in Figure 4 with that for $\langle \rho \rangle$ given in Figure 1. Previously using quasielastic neutron scattering (QENS) and atomistic MD simulation, we have demonstrated that the internal relaxation of polymer components of a dendrimer was indeed driven by their interaction with invasive water:[17] More invasive water results in faster relaxation. Therefore, it is reasonable to see the connection between the slowing down of internal relaxation and the molecular dehydration. Because both τ_{intra} and τ_{inter} showed in Figure 4 evolve continuously in opposite direction, the intersection of evolving τ_{intra} and τ_{inter} must exist which is considerably less than the geometrically defined c^*. Assuming both τ_{intra} and τ_{inter} evolve exponentially as a function of c, c_D^* of G4 and G6 dendrimers are found to be around 10 wt %. The physical meaning of c_D^* is that it marks a dynamically defined threshold of diluteness. Below c_D^* the interdendrimer collision time τ_{inter} is statistically longer than the internal relaxation time, τ_{intra}, so that the majority of dendrimers recover their original conformation after collision. However, beyond c_D^*, the majority of dendrimers have no time to recover, and as a result retain their deformed states induced by interparticle collisions.

In conclusion, by means of neutron scattering, we investigate the conformational and dynamical behavior of a dendrimer, a model soft colloidal system, as a function of particle concentration, below the overlap concentration c^*. Previous studies show that within this concentration range the size of soft colloids remains invariant.[8] This observation leads to the general understanding that within this dilute regime the colloidal conformation remains unperturbed and that conformational evolution occurs only when $c > c^*$. However, we demonstrate that significant dehydration and progressively slowing down of internal collective motions are observed before the intercolloidal physical overlap develops. The origin of these unexpected conformational and dynamical changes below c^* is the interplay between the inter- and intraparticle relaxation processes influenced by increasing concentration. Since this dynamical effect, crucial to understanding soft colloids, is not incorporated in the geometric definition of c^*, the observed characteristic conformational and dynamical evolutions when c

$< c^*$ suggest that c^* is not a suitable index parameter for defining the threshold for diluteness in these systems. Instead, a different dilute threshold concentration c_D^* naturally emerges from the crossover of the relaxation times associated with these two competing dynamical processes. Below c_D^* the conformation and internal dynamics are free from the influence of interparticle collision, whereas above c_D^* they are strongly modified by collision. Therefore, c_D^* serves a proper threshold of diluteness with the incorporation of dynamical effect. In the scaling theory of polymer the threshold of diluteness has been among the most important characteristic parameters. Nevertheless, the dynamical effect was never previously considered in various forms of its definitions. Since all polymer solutions are generally characterized by various thermally driven diffusion processes, our finding suggests that it is a promising area for future research to investigate its dynamical dependence for polymers of different architectures. Moreover, we show that both G4 and G6 dendrimers, with different degrees of structural softness,[13a] exhibit qualitatively similar conformational and dynamical evolutions below c^*, suggesting the possibility of a universal behavior. It will be therefore intriguing to explore whether other soft colloidal systems consisting of tethered chains, such as star polymers and grafted nanoparticles, are also characterized by a similar dynamical crossover. Finally, in the limit of a stiff particle (hard sphere) its c_D^* is identical to c^*. Therefore, the difference between c_D^* and c^* provides a new quantitative parameter for describing the degree of "softness" in this important class of soft matter.

■ ASSOCIATED CONTENT

⑤ Supporting Information

(1) Sample preparations; (2) Packing of invasive water; (3) SANS experiment and data analysis; (4) NSE experiment and data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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