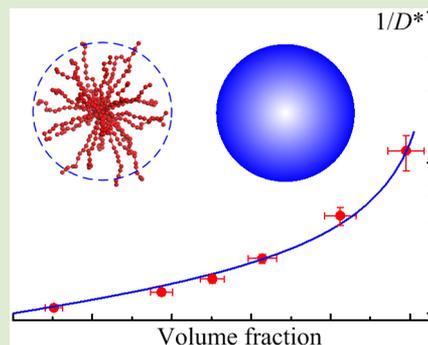


Dynamic Equivalence between Soft Star Polymers and Hard Spheres

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Supporting Information

ABSTRACT: Understanding the dynamics of soft colloids, such as star polymers, dendrimers, and microgels, is of scientific and practical importance. It is known that the excluded volume effect plays a key role in colloidal dynamics. Here, we propose a condition of compressibility equivalence that provides a simple method to experimentally evaluate the excluded volume of soft colloids from a thermodynamic view. We apply this condition to survey the dynamics of a series of star polymer dispersions. It is found that, as the concentration increases, the slowing of the long-time self-diffusivity of the star polymer, normalized by the short-time self-diffusivity, can be mapped onto the hard-sphere behavior. This phenomenon reveals the dynamic equivalence between soft colloids and hard spheres, despite the apparent complexity of the interparticle interaction of the soft colloids. The methods for measuring the osmotic compressibility and the self-diffusivities of soft colloidal dispersions are also presented.



Dispersions of soft deformable colloids, such as star polymers, dendrimers, microgels, and polymer-grafted nanoparticles, constitute a great portion of soft matters.^{1–4} These materials exist extensively in the fields of food, pharmaceutical, and chemical engineering. Therefore, measuring and modeling their physical properties are of practical importance. A fundamental challenge in the physics of soft colloids is to quantitatively predict the slowing of their long-time dynamics as the concentration increases, since this behavior is closely related to many essential phenomena, for example, the phase behavior, glass formation, and rheology.^{3–8} Over past decades, several theoretical and computational efforts have been made on this topic.^{9–14} In these studies, researchers introduced the effective volume fraction ϕ_{eff} (or effective diameter $d_{\text{eff}} = (\phi_{\text{eff}}/n\pi)^{1/3}$, where n is the number density of particles) for soft particles due to their excluded volume effect at high concentrations. With ϕ_{eff} , the long-time dynamics of soft particles can be scaled to the hard-sphere behavior,^{10–13} which is well investigated both experimentally and theoretically.¹⁵ The key prerequisite for these scaling operations is the pair potential $v(r)$ ¹⁰ (r is the distance between two colloids) or the interparticle structure factor $S(Q)$ ^{11–13} (Q is the magnitude of the scattering vector in scattering experiments) of the soft colloids. However, without knowing the exact way how the particle deforms as

concentration increases and an accurate functional form of the pair potential at high concentrations, it is very difficult to measure $v(r)$ and $S(Q)$ precisely from scattering experiments, especially at high concentrations. To address this problem from an experimental perspective, we propose a condition of compressibility equivalence that provides a remarkably simple way to determine the effective volume fraction of soft colloids from the small-angle neutron scattering (SANS) experiment. Employing this condition, we find that the slowing of the long-time self-diffusion of soft colloids can be nicely mapped onto the property of hard spheres.

A series of star polymer dispersions are measured to study the dynamics of colloidal liquids with soft repulsive interactions. Star polymers are synthetic macromolecules consisting of polymeric branches emanating from the molecular center. Experimental and theoretical studies show that star polymers exhibit colloidal nature in dispersions.^{2,16–20} Due to their flexible molecular architecture, the effective potential between two stars has been modeled as an ultrasoft repulsion.^{21,22} In this work, 15-arm polystyrene stars, with on

Received: August 8, 2019

Accepted: September 12, 2019

Published: October 15, 2019

average 12.5 monomers contained in each arm, are used as the model soft deformable colloids. Cyclohexanone is adopted as the good solvent. Six concentrations of stars, 3, 10, 15, 20, 30, and 40 wt % (wt % indicates the weight fraction in percent), are investigated. Figure 1 displays the SANS spectra of the stars

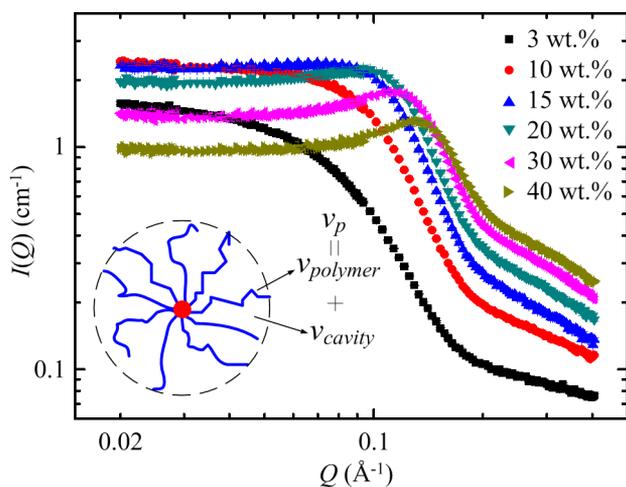


Figure 1. SANS spectra of the star polymer dispersions at six measured concentrations. The inset illustrates the meaning of v_p , v_{polymer} and v_{cavity} in a star polymer dispersion.

at the above six concentrations. Upon increasing the concentration, the interaction peak grows gradually up to about 15 wt % and then decays with a further concentration increment. This nonmonotonic evolution of the main peak has been identified as the generic feature of soft colloidal systems,^{2,23} and its origin has been attributed to the diminishing density fluctuation at the molecular level due to the increasing mutual interaction.^{21,24} Notice that this behavior is significantly different from the behaviors of hard spheres, where the interaction peak progressively grows as concentration increases.¹⁵

It is instructive to briefly review a few theoretical results before further analysis. There are two well-defined self-diffusive processes in colloidal suspensions: the short-time self-diffusivity D_{SS} and the long-time self-diffusivity D_{LS} .^{5,8,25–28} D_{SS} describes the diffusion of the particle within its neighbor cage, while D_{LS} describes the self-diffusion on a time scale longer than that of the local structural rearrangement.^{25,26} At the dilute limit, both of them equal the Stokes–Einstein diffusivity of an isolated particle: $D_0 = kT/3\pi\eta_s a$, where k is the Boltzmann constant, T is the temperature, η_s is the solvent viscosity, and a is the hydrodynamic diameter of the particle. As the concentration increases, D_{SS} is retarded due to the emergence of the hydrodynamic interaction.^{5,27} In the long-time self-diffusion, the tagged particle breaks the neighbor cage and moves to relatively distant places. This process requires the distortion and relaxation of the local configuration.^{25,26} As concentration increases, it slows down more significantly than the short-time self-diffusion due to the excluded volume effect of particles. Considering that the mechanisms of the slowing of D_{SS} and D_{LS} are distinct and the time scales of D_{SS} and D_{LS} are well separated at high concentrations, theorists point out that D_{LS} can be approximately factorized into a hydrodynamic part and a thermodynamic or structural part, namely,^{25,26}

$$D_{LS} \approx D_{SS} f(S(Q)) \quad (1)$$

where $f(S(Q))$ is a factor depending on the properties of $S(Q)$ (or the pair distribution function $g(r)$). Therefore, it is natural to introduce a normalized long-time self-diffusivity $D^* = D_{LS}/D_{SS}$ to characterize the long-time dynamics of the star polymers. D_{SS} , on the other hand, plays a role as a coarse-grained time resolution. We would like to point out that the influence of hydrodynamic interaction on D_{LS} is more complicated than the decoupling approximation given by eq 1.^{28–31} Nevertheless, we argue that D^* is a proper quantity that reflects the thermodynamic or structural basis of the long-time self-diffusion of colloids, by considering that (i) the drastic slowing of D_{LS} as the concentration increases is mainly due to the structure rather than the hydrodynamic interaction and (ii) the approximation given by eq 1 explains experimental data well, as suggested in refs 25 and 26. In the following analyses, we will use D^* as a measure of the long-time dynamics of the star polymers.

To describe the dynamics of soft particles with hard-sphere properties, it is crucial to find the effective volume fraction ϕ_{eff} for soft particles based on certain structural or thermodynamic similarities between these two systems. Inspired by previous theoretical results,^{9–13} we propose that, for a soft repulsive colloidal dispersion with the number density of colloids n , ϕ_{eff} is determined by the following condition:

$$\lim_{Q \rightarrow 0} S_{sc}(Q; n) = \lim_{Q \rightarrow 0} S_{hs}(Q; n, \phi_{\text{eff}}) \quad (2)$$

where $S_{sc}(Q; n)$ is the interparticle structure factor of the soft colloidal dispersion with number density of n , $S_{hs}(Q; n, \phi_{\text{eff}})$ is the structure factor of the monodisperse hard-sphere system with number density of n and volume fraction of ϕ_{eff} . Since $S(Q \rightarrow 0)$ is related to the osmotic compressibility χ of colloidal dispersions by $S(Q \rightarrow 0) = nkT\chi$,^{15,32} we call eq 2 as the condition of compressibility equivalence. This equivalence suggests that the two systems bear a resemblance to each other regarding the effect of the excluded volume of all particles. In fact, for liquids with purely repulsive potential, χ is largely determined by the second virial coefficient that gives the excluded volume of a particle in the van der Waals picture. In eq 2, $S_{hs}(Q; n, \phi_{\text{eff}})$ can be calculated with Percus–Yevick approximation³³ and Verlet–Weis correction.³⁴ Thus, ϕ_{eff} can be obtained when $S_{sc}(Q \rightarrow 0; n)$ is known. In the following part, we will show that, with ϕ_{eff} defined by eq 2, the D^* of star polymers is found to be equivalent to that of the hard spheres.

The theoretical foundation of eq 2 is similar to the scheme proposed by Xu et al.⁹ With a computer simulation, these authors investigated many soft-core liquids. Some of them are with very soft interactions, such as harmonic repulsion. They found that at low pressures, the dynamics of soft-core liquids and hard-sphere liquids can be collapsed to a single curve as a function of T/Pd^3 , where P is pressure and d is the diameter of the soft repulsion. By employing eq 2 at all concentrations, we ensure that the soft particles and hard spheres have a common $dP/d\phi_{\text{eff}}$ in the case that d_{eff} does not change too much as concentration increases. Consequently, the soft particles and hard spheres are with similar equations of state, that is, the pressure as a function of volume fraction. Therefore, the condition of compressibility equivalence leads to comparable dynamical properties of soft particles and hard spheres according to the scheme given by Xu et al. Nevertheless, this dynamic scaling fails at high pressures or concentrations due to the overlap between soft particles. Further investigation suggests that this scaling can be improved and extended to

systems with ϕ_{eff} well above 50% by considering the shrink of the effective volume of particles at high pressures or concentrations.¹⁰

Another scheme, proposed by Medina-Noyola et al., states that the ϕ_{eff} determined by the following condition, maps the long-time self-diffusion of soft colloids onto that of hard spheres:^{11–13}

$$S_{\text{sc}}(Q; n) \approx S_{\text{hs}}(Q; n, \phi_{\text{eff}}) \quad (3)$$

The symbol “ \approx ” in the preceding equation means that the two structure factors match at low and intermediate Q , corresponding to the main peak of $S(Q)$.^{11–13,35,36} In real space, eq 3 indicates that the pair distribution functions $g(r)$ of the two systems are approximately equal at $r > \sim 1.3d_{\text{eff}}$.^{15,36} It emphasizes the similarity of the overall nature of packing rather than the details at the contact of the two systems. Therefore, we arguably state that the physical backgrounds of eqs 2 and 3 are consistent.

To experimentally measure D^* of soft colloids and verify its possible equivalence to the hard-sphere behavior, one needs to probe $S_{\text{sc}}(Q \rightarrow 0)$, D_{SS} , and D_{LS} . We devise a model-independent method using the contrast-variation SANS to find $S_{\text{sc}}(Q \rightarrow 0)$. For a monodisperse colloidal dispersion,³⁷ the SANS spectrum is expressed as³⁸

$$I(Q) = nv_{\text{p}}^2(\Delta\rho^{\text{sld}})^2P(Q)S(Q) \quad (4)$$

where n is the number density of colloid particles, v_{p} is the volume occupied by one colloidal particle, $\Delta\rho^{\text{sld}}$ is the contrast of the scattering length density (sld) between the colloidal particle and the solvent, and $P(Q)$ is the form factor of a colloidal particle normalized as $P(0) = 1$. At zero scattering angle, the SANS intensity of the star polymer dispersion is written as

$$I_{\gamma}(Q \rightarrow 0) = n[v_{\text{p}}\Delta\rho^{\text{sld}}(\gamma)]^2S_{\text{sc}}(Q \rightarrow 0) \quad (5)$$

where γ is the fraction of deuterated component in the solvent. For soft colloidal liquids, v_{p} contains two parts, the n -independent volume of the dry polymer (v_{polymer}) and the n -dependent volume of the cavity (v_{cavity}), as illustrated in the inset of Figure 1.^{39,40} Here we denote the contrast of the scattering length in the volume of v_{p} as $b(\gamma)$. It can be found that

$$b(\gamma) = v_{\text{p}}\Delta\rho^{\text{sld}}(\gamma) = b_{\text{polymer}} - \rho_{\text{sol}}^{\text{sld}}(\gamma)[v_{\text{polymer}} + v_{\text{cavity}}(n) - v_{\text{cavity}}(n)v_{\text{sol}}h(n)] \quad (6)$$

where b_{polymer} is the scattering length of a star, $\rho_{\text{sol}}^{\text{sld}}$ is the sld of the solvent, v_{sol} is the volume of a solvent molecule, and h is the number density of the solvent molecule in the cavity. The justification of eq 6 is given in ref 41. Combining eqs 5 and 6, it is found that

$$\sqrt{\frac{I_{\gamma}(Q \rightarrow 0)}{n}} = -\rho_{\text{sol}}^{\text{sld}}(\gamma)L(n)\sqrt{S_{\text{sc}}(Q \rightarrow 0)} + b_{\text{polymer}}\sqrt{S_{\text{sc}}(Q \rightarrow 0)} \quad (7)$$

where $L(n) = v_{\text{polymer}} + v_{\text{cavity}}(n) - v_{\text{cavity}}(n)v_{\text{sol}}h(n)$. The preceding equation shows the linear relation between $\sqrt{I_{\gamma}(Q \rightarrow 0)/n}$ and $\rho_{\text{sol}}^{\text{sld}}(\gamma)$. By measuring the samples with different γ and plotting $\sqrt{I_{\gamma}(Q \rightarrow 0)/n}$ as a function of $\rho_{\text{sol}}^{\text{sld}}(\gamma)$, $S_{\text{sc}}(Q \rightarrow 0)$ can be obtained from the vertical intercept. Figure 2 illustrates this method. The experimentally determined $S_{\text{sc}}(Q$

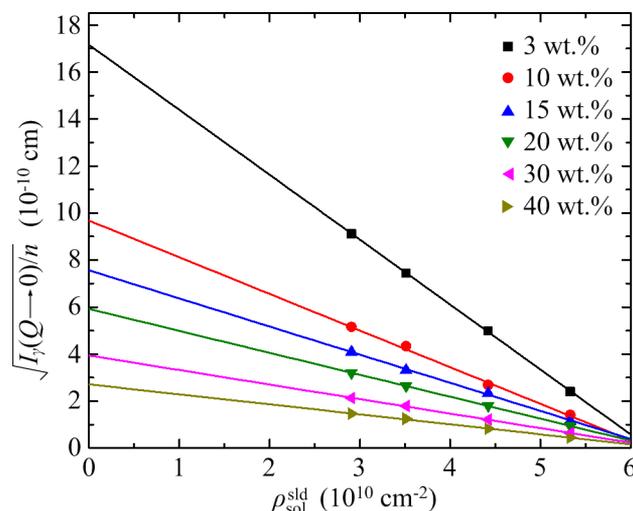


Figure 2. Illustration of the contrast-variation SANS method for the determination of $S_{\text{sc}}(Q \rightarrow 0)$. In this study, we prepared four solvents at $\gamma = 40\%$, 50% , 65% , and 80% for each concentration. Deuterated star polymers were used to reduce the incoherent background. The symbols represent the experimental data. The lines are from the linear fitting with eq 7. The adjusted R^2 values of all fittings are above 0.995, indicating a good linearity between $\sqrt{I_{\gamma}(Q \rightarrow 0)/n}$ and $\rho_{\text{sol}}^{\text{sld}}(\gamma)$.

$\rightarrow 0$) for the measured concentrations, from low to high, are 0.665, 0.235, 0.143, 0.0877, 0.0388, and 0.0184. Then applying eq 2, we obtain the values of ϕ_{eff} to be 0.051, 0.18, 0.25, 0.31, 0.41, and 0.49, respectively.

Traditionally, people use dynamic light scattering to measure the self-diffusivities of hard-sphere colloids at high Q regions.^{8,27} However, it cannot be applied to star polymers, since the local motions, such as the rotational diffusion and intramolecular motion, are prominent. Here we use the Neutron Spin Echo (NSE) spectrometer with a contrast-match method to measure the short-time self-diffusion of star polymers. We measured the samples at $Q = 0.04 \text{ \AA}^{-1}$ to determine D_{SS} . This Q value is much smaller than $2\pi/R_{\text{g}}$ ($R_{\text{g}} = 19 \text{ \AA}$ is the radius of gyration of a star), so that the dynamical contribution of local motions is much less than that of the translational diffusion and thus can be reasonably ignored. To obtain the self-dynamics of the star, we prepared the samples composed of a fixed concentration of 3 wt % protonated star with progressively increasing concentration of fully deuterated stars immersed in solvent whose sld matches that of fully deuterated stars. Because the fraction of protonated stars is relatively dilute, the NSE signal is mainly from the self-motion of a star. The D_{LS} was measured with the diffusion Nuclear Magnetic Resonance (NMR) spectroscopy on the same set of samples. Both the measured results of D_{SS} and D_{LS} are shown in Figure 3.⁴²

Knowing D_{SS} , D_{LS} , and ϕ_{eff} we are able to explore the equivalence in colloidal dynamics. In Figure 4a, we plot $1/D^*$ as a function of ϕ_{eff} for the star polymer dispersion. We also plot $1/D^*$ as a function of the volume fraction for hard spheres. The hard-sphere equation is obtained from the least-squares fit of the Brownian dynamics simulation:⁴⁴

$$D^* = 1 - 2\phi + 1.272\phi^2 - 1.951\phi^3 \quad (8)$$

It is proven that this form nicely describes the simulations and experimental measurements.⁴⁴ From Figure 4a, an excellent agreement between the experimental result and the

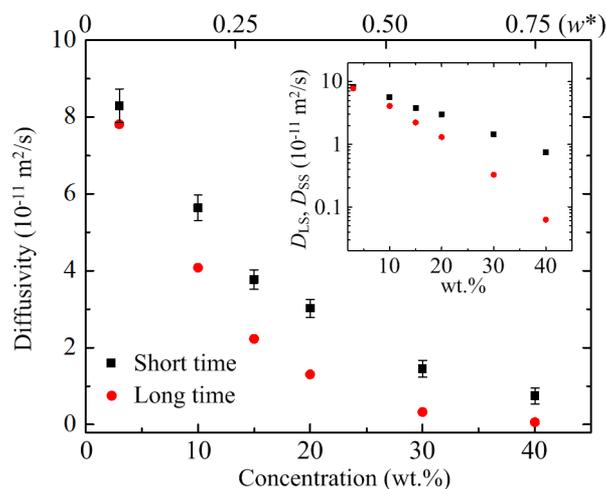


Figure 3. Measured short-time and long-time self-diffusivities of the star polymer dispersions as a function of concentration. The upper horizontal scale is in unit of the overlap concentration w^* .⁴³ The inset presents the diffusivities in logarithmic scale.

hard-sphere behavior is seen, which verifies the dynamic equivalence between the soft star polymers and the hard spheres. This observation highlights the effects of excluded volume and overall packing of particles in determining the long-time dynamics of soft colloids. Furthermore, it supports the theoretical conjecture that D^* is not affected by the solvent permeability in soft colloidal suspensions.⁴⁴ To make a comparison, we calculate an “apparent volume fraction” of the star, which is defined as $\phi' = 4n\pi R_g^3/3$ and has been used in previous studies of soft particles.⁶ The result is presented in the inset of Figure 4a. As seen, the experimental points systematically deviate from the hard-sphere prediction. This deviation suggests that R_g underestimated the excluded volume of soft particles. A similar situation happens to another definition of volume fraction expressed as $\phi'' = n\pi\sigma^3/6$,⁴⁵ where σ is the corona diameter of a star and is related to R_g by $\sigma \approx 1.26R_g$.²² ϕ'' is found to be even smaller than ϕ' at the same concentration and, therefore, again underestimates the excluded volume of the star in terms of the long-time self-dynamics. We also evaluate the volume fraction with the hydrodynamic radius R_h by $\phi_h = 4n\pi R_h^3/3$. R_h is estimated by noting the experimental result that the value of R_h is close to σ .⁴⁶ The result is shown in the inset of Figure 4a. It is seen that ϕ_h overestimates the excluded volume of the star at concentrations higher than 15 wt %.

An important observation is the evolution of d_{eff} as concentration increases. As shown in Figure 4b, d_{eff} is approximately equal to the hydrodynamic diameter a_h at the lowest concentration. It starts decreasing slightly from a concentration about 15 wt %, corresponding to the number density of star polymers of $n' = 5.14 \times 10^{18} \text{ cm}^{-3}$. This shrink of d_{eff} at high concentrations (or pressure) is similar to previous simulations.¹⁰ It is interesting to compare n' with the overlap number density n^* defined as

$$n^* \approx \phi_{\text{RCP}} / \frac{4}{3} \pi R_g^3 \quad (9)$$

where $\phi_{\text{RCP}} = 0.637$ is the random-close-packing volume fraction.⁴⁷ Note that, in other studies, n^* is usually defined as $n^* \approx 3/4\pi R_g^3$.^{48,49} These definitions are within the same order. n^* calculated with eq 9 is $2 \times 10^{19} \text{ cm}^{-3}$, which is much larger

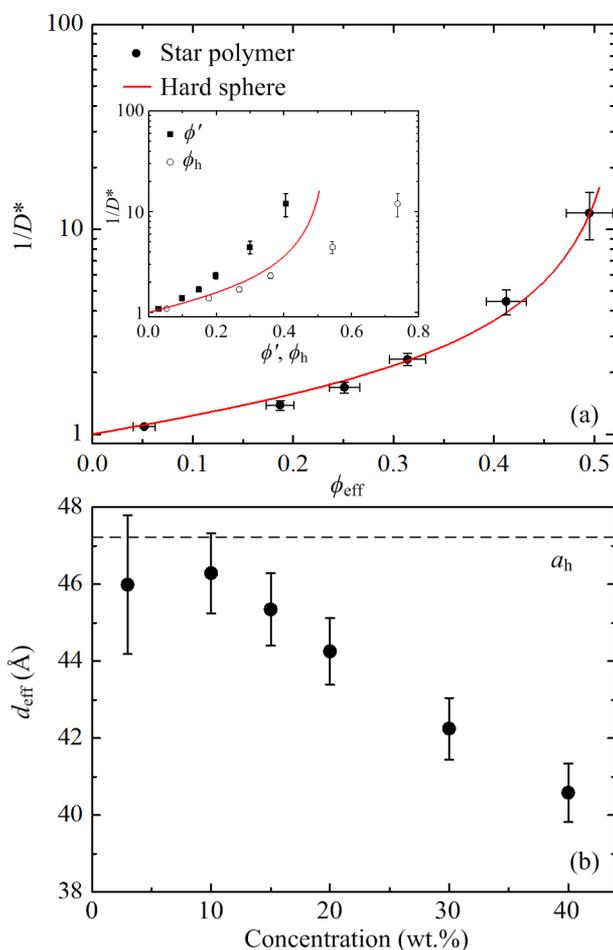


Figure 4. (a) $1/D^*$ as a function of ϕ_{eff} . The symbols represent the experimental result of the star polymer dispersion. The line represents a theoretical calculation for hard spheres.⁴⁴ It is seen that the hard-sphere curve gives an excellent prediction to the behavior of the star polymer dispersion. The inset gives the results with two different methods for determining the volume fraction of star polymer: $\phi' = 4n\pi R_g^3/3$, $\phi_h = 4n\pi R_h^3/3$. (b) Effective diameter of the star d_{eff} as a function of concentration. d_{eff} is related to ϕ_{eff} by $\phi_{\text{eff}} = n\pi d_{\text{eff}}^3/6$. The dashed line indicates the value of the hydrodynamic diameter a_h .

than n' . The same conclusion can be drawn by calculating n^* using $d_{\text{eff}}/2$ or $\sigma/2$ instead of R_g . The difference between n' and n^* suggests that the star undergoes conformational change before the physical overlap develops. This result is consistent with our previous study on dendrimer solutions.⁵⁰

Actually, seeking for the analogy between hard-sphere and soft-core liquids has been an essential topic in liquid physics since at least 50 years ago.⁵¹ It was shown that the intermolecular structure of liquids with strongly isotropic repulsive potential can be understood in terms of the packing of equivalent hard-sphere systems.³⁵ The perturbation theory built on this idea successfully describes the structure and thermodynamics of Lennard-Jones liquids.⁵² The hard sphere–soft core analogy has also been observed in dynamic properties in simulations.^{9,13,53} Notice that, other scaling scenarios have been given for temperature-driven liquid–glass transition, where hard-sphere properties do not play a substantial role.^{54–56} To summarize various liquids’ universal behaviors, Dyre et al. proposed a concept of isomorph for liquids,^{57–59} which suggests that the liquids have nearly the same structure and dynamic correlation functions if they are isomorphic. This

scaling works well for liquids with inverse-power-law potentials and also for hard-sphere and Lennard-Jones systems. Our result is generally consistent with this scenario. A special feature of this work is the way to determine ϕ_{eff} . Compared with other methods,^{10,11,60,61} eq 2 can be directly accessed by SANS measurements for colloidal suspensions without knowing the functional form of interparticle potential. Therefore, it could be of particularly importance for the experimental investigation on colloidal systems.

This work, as well as many previous studies on soft core–hard sphere dynamic analogy, assumes that the dynamics is fully determined by structure. The relevant structural parameter and dynamics evolve monotonically as concentration increases in the studied region. However, the situation at concentrations higher than the overlap concentration could be complicated. Simulation and experiment show that near the jamming point the dynamics and structure of soft-core particles exhibit uncommon discrepancies.⁶² A recent study suggests that the crossing of the barriers in the energy landscape needs to be considered in finding the effective volume fraction.⁶³ Moreover, recent simulations found that ultrasoft colloids exhibit re-entrant glass transition above the overlap concentration.^{64–66} These findings indicate that the strong overlap between soft particles leads to unusual dynamical behaviors.

We notice that a computer simulation study reports that the ultrasoft potential developed for star polymers²² violates the hard sphere–soft core dynamic analogy.⁶⁷ The inconsistency between the simulation and our result is probably due to two reasons. First, our samples have a small number of monomers on each arm, which is not perfectly consistent with the physical background of the ultrasoft potential. Second, the theoretical potential form underestimates the excluded volume of the star at finite concentrations. In fact, the SANS spectrum calculated with the ultrasoft potential exhibits a higher Q_{max} (Q_{max} is the position of the main peak of $S(Q)$) and a lower intensity compared with the measured spectrum at intermediate concentrations, as shown in Figure 2 of ref 22. This indicates that the theoretical potential underestimates the strength or the range of exclusion of the interparticle interaction.

In conclusion, we measure star polymer dispersions to study the dynamics of soft colloidal liquids. We find that the slowing of the long-time self-diffusivity, normalized by the short-time self-diffusivity, can be scaled to the hard-sphere behavior with an effective volume fraction, determined using the condition of compressibility equivalence. This result provides a new insight in understanding the long-time self-diffusion of soft colloids from a thermodynamic view. In addition, we give a simple method to determine the osmotic compressibility of soft colloidal liquids with SANS.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00617.

Detailed descriptions of the Neutron Spin Echo experiments and the contrast-variation SANS results (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to Dr. J. F. Douglas for valuable discussion. We acknowledge the support of NIST Center for Neutron Research, Spallation Neutron Source at Oak Ridge National Laboratory, and Institut Laue-Langevin, in providing the neutron research facilities, and the NMR facility at the University of Arizona in performing the NMR measurements. Access to Neutron Spin Echo and SANS at NIST was provided by the Center for High Resolution Neutron Scattering, a partnership between the National Institute of Standards and Technology and the National Science Foundation under Agreement No. DMR-1508249. This research at SNS of Oak Ridge National Laboratory was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. The research at Tsinghua University was supported by the Starting Grant from Tsinghua University.

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- (37) The flexibility of the soft polymeric particle may lead to dynamic polydispersity. However, for our sample, there are only 12 monomers in one arm, so that the flexibility should be weak. Moreover, we use a good solvent that can enhance the rigidity of the arm. Thus, the dynamic polydispersity of the volume of the star polymer should be very small.
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- (41) Equation 6 can be justified as follows: $(h\nu_{\text{cavity}})v_{\text{sol}}$ is the volume occupied by solvent molecules in the cavity, and $\rho_{\text{sol}}^{\text{slid}}(h\nu_{\text{cavity}})v_{\text{sol}}$ is the contribution of the invasive solvent molecules to the scattering length in v_{p} . Thus, the total contribution of the star polymer and invasive solvent to the scattering length in v_{p} is $b_{\text{polymer}} + \rho_{\text{sol}}^{\text{slid}}h\nu_{\text{cavity}}v_{\text{sol}}$. By subtracting the solvent background, $\rho_{\text{sol}}^{\text{slid}}v_{\text{p}}$, one finds the contrast of the scattering length in v_{p} expressed by eq 6. Note that, here we assume that $\rho_{\text{sol}}^{\text{slid}}$ does not change from the bulk phase to the invasive phase. Actually, this assumption does not affect the analysis. Considering that the density of the invasive solvent is different from that of the bulk solvent by a factor of $f(n_{\text{p}})$ at a specific concentration, n_{p} , we can fix the above quantity by writing $\rho_{\text{sol}}^{\text{slid}}(n_{\text{p}})h(n_{\text{p}})v_{\text{cavity}}(n_{\text{p}})v_{\text{sol}}\text{bef}(n_{\text{p}})$ can be absorbed into $h(n_{\text{p}})$, and then the same expression retains.
- (42) See Supporting Information for detailed descriptions of the NSE experiments and the contrast-variation SANS.
- (43) The overlap concentration $w^* \approx 53$ wt % gives the weight percent of the star polymer at the overlap number density defined in eq 9.
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