Observation of the Dynamic Equivalence between Soft Star Polymers and Hard Spheres via Compressibility Scaling

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We propose a definition of the effective hard-sphere volume fraction \( \phi_{HS} \) for liquids composed of soft repulsive particles by employing the condition of compressibility equivalence, and devise a model-independent method to determine \( \phi_{HS} \) for soft colloids from Small-Angle Neutron Scattering (SANS) experiments. A series of star polymer dispersions are measured as a model soft colloidal liquid. It is found that as the concentration increases, the slowing of the long-time dynamics of the star polymer, normalized by the short-time self-diffusion coefficient, can be scaled to the hard-sphere behavior with \( \phi_{HS} \). This result agrees with the dynamic equivalence rule between the soft-repulsive and hard-sphere colloidal liquids predicted by recent theoretical and simulation work.

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Hard-sphere (HS) system plays a crucial role in both the theories of simple liquids \[1\] and colloidal suspensions \[2\]. It has been accepted that \[3–7\], for a liquid with a soft-repulsive (SR) interparticle potential and a number density \( \rho_{SR} \), its static structure factor \( S_{SR}(Q) \) can be reasonably represented by a HS form, known as the principle of structural equivalence:

\[
S_{SR}(Q) \approx S_{HS}(Q; \rho_{HS}, \phi_{HS}), \tag{1}
\]

where \( \phi_{HS} \) and \( \rho_{HS} \) are the effective HS volume fraction and number density of the SR liquid, respectively \[8\]. For SR potentials with a weak or moderate softness, it is found that \( \rho_{SR} \approx \rho_{HS} \). Equation 1 can be understood as a result of the excluded volume effect of the liquid particles, as suggested by the well-known fact that the equilibrium structure of a liquid is mainly determined by its short-range repulsion in the interparticle potential \[1, 9\]. The relation given by Eq. \( 1 \) has profound implications on the colloidal dynamics. According to the self-consistent generalized Langevin equation (SCGLE) theory developed by Medina-Noyola \etal \[10\], the time-dependent density autocorrelation function \( F(Q, t) \) (or its self part) of a colloidal liquid is just determined by \( S(Q) \) and \( \rho \). This is similar to the result of the mode coupling theory \[15\] that describes simple liquid dynamics. In this framework, the structural equivalence directly leads to the dynamic equivalence \[16\]:

\[
F_{SR}(Q, t_{SR}^*) \approx F_{HS}(Q, t_{HS}^*; \rho_{HS}, \phi_{HS}), \tag{2}
\]

where \( t_{SR/HS}^* \) is the time scaled by the short-time self-diffusion coefficient \( D^{(SS)}; t_{SR/HS}^* = D^{(SS)}/D_{SR/HS} \). This scaling gives a coarse-grained time-resolution corresponding to several collisions. The theoretical prediction in Eq. 2 has been verified by Brownian dynamics (BD) studies on systems with various SR interparticle potentials \[18\]. In fact, the BD data suggest more fascinating results. It is found that, Eq. 2 works well even for systems with very soft and long-ranged potentials, such as the Yukawa potential with a hard core \[10\]. More strikingly, it is shown that the establishment of the dynamic equivalence can be built on a much less-restricted condition than Eq. 1, namely \[10\]:

\[
S_{SR}(Q \rightarrow 0) = S_{HS}(Q \rightarrow 0; \rho_{HS}, \phi_{HS}). \tag{3}
\]

We call Eq. \( 3 \) the condition of compressibility equivalence due to the proportionality between \( S(Q \rightarrow 0)/\rho \) and the isothermal (or osmotic) compressibility \( \chi \). \( \chi \) measures the liquid’s resistance to the compression, and thus is closely related to the excluded volume effect of particles. To be specific, for simple liquids with a purely repulsive potential, the isothermal compressibility is largely determined by the second Virial coefficient, which is just the excluded volume of a particle in the van der Waals picture. Similar conclusion can be found for colloidal suspensions. Considering these views, we argue that Eqs. 1 and 3 share a common physical foundation. Equation 3 is of great value to the experimental study on colloidal dynamics: Firstly, the determination of \( S(Q \rightarrow 0) \) of a colloidal suspension is much easier than that of the \( S(Q) \), which usually requires nonlinear fit with certain models and assumptions. Moreover, for many soft colloids, the condition of compressibility equivalence can
be realized while the structural equivalence cannot, as demonstrated below. Henceforth, we will use Eq. 3 as the definition of $\phi_{HS}$ of soft colloids.

There has been much interest in understanding the mechanism of the slowing of the colloidal dynamics as the concentration $c$ (or volume fraction) increases due to its crucial role in the formation of colloidal glass. Extensive experiments have shown that during this process the colloidal liquids with different interactions exhibit different fragilities [20, 23]. The predicted dynamic equivalence suggests that, despite the apparent complexity, the slowing of the long-time self-diffusion coefficient $D^{(SSS)}$ of SR colloidal liquids, normalized by $D^{(SSS)}$, is equivalent to the HS behavior by scaling with $\phi_{HS}$ [10, 18].

A permanent question, however, refers to the range of experimental validity of this picture, particularly regarding the softness of the interaction. Experimentally testing this scaling rule is highly non-trivial, since one has to probe both, the structure and the dynamics, of a colloidal system formed by considerably soft particles. In this work, we measure a series of star polymer dispersions at 6 measured concentrations. The inset illustrates the meaning of $v_p$, $v_{\text{polymer}}$ and $v_{\text{cavity}}$ in a star polymer dispersion.

![FIG. 1. The SANS spectra of the star polymer dispersions at 6 measured concentrations. The inset illustrates the meaning of $v_p$, $v_{\text{polymer}}$ and $v_{\text{cavity}}$ in a star polymer dispersion.](Image)

For a monodisperse colloidal suspension, the measured SANS spectrum is expressed as [31]:

$$I(Q) = n_p v_p^2 (\Delta \rho_{\text{sol}}^s)^2 P(Q) S(Q),$$

where $n_p$ is the number density of colloid particles, $v_p$ is the volume occupied by one colloidal particle, $\Delta \rho_{\text{sol}}^s$ 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 $P(0) = 1$. Figure 1 displays the $I(Q)$ of the protonated stars immersed in fully deuterated solvents at 6 measured $c$: 3, 10, 15, 20, 30 and 40 wt.% (weight percent). Upon increasing $c$, the peak intensity increases when $c < 15\%$ but decrease when $c > 15\%$. This behavior has been identified as the generic feature of soft colloidal liquids [27, 28] and its origin has been attributed to the diminishing density fluctuation at molecular level due to the increasing interpenetration [25, 32]. Notice that, such a non-monotonic evolution of $I(Q)$ is different from the HS behaviors. Thus, the condition given by Eq. 1 cannot be applied to soft colloids at high $c$.

To obtain $\phi_{HS}$ defined in Eq. 3, we devise a methodology using the contrast-variation SANS. At zero scattering angle, the SANS intensity of the star polymer dispersion is expressed as:

$$I_s(Q \to 0) = n_p [v_p (\Delta \rho_{\text{sol}}^s)^2] S_{SR}(Q \to 0),$$

where $\gamma$ is the ratio of deuterated component in the solvent. For soft colloidal liquids, $v_p$ contains two parts, the $n_p$-independent volume of the dry polymer $v_{\text{polymer}}$ and the $n_p$-dependent volume of the cavity $v_{\text{cavity}}$, as illustrated in the inset of Fig. 1 [33, 34]. Here we denote the contrast of the scattering length in $v_p$ as $b(\gamma)$. It can be found that:

$$b(\gamma) = v_p (\Delta \rho_{\text{sol}}^s)^2 = b_{\text{polymer}} - \rho_{\text{sol}}^s (\gamma) \times [v_{\text{polymer}} + v_{\text{cavity}}(n_p) - v_{\text{cavity}}(n_p) v_{\text{sol}} h(n_p)],$$

where $b_{\text{polymer}}$ is the scattering length of a star, $\rho_{\text{sol}}^s$ is the sld of the solvent, $v_{\text{sol}}$ is the volume of a solvent molecule, and $h$ is the number density of the solvent molecule in the cavity. Equation 6 can be justified as follows: $(h v_{\text{cavity}}) v_{\text{sol}}$ is the volume occupied by solvent molecules in the cavity, and $\rho_{\text{sol}}^s (h v_{\text{cavity}}) v_{\text{sol}}$ is the contribution of the invasive solvent molecules to the scattering length in $v_p$ [37]. Thus, the total contribution of the star polymer and invasive solvent to the scattering length in $v_p$ is $b_{\text{polymer}} + \rho_{\text{sol}}^s h v_{\text{cavity}} v_{\text{sol}}$. By subtracting
the solvent background $\rho_{\text{sol}}^d v_p$, one gets the contrast of the scattering length in $v_p$ expressed by Eq. 6.

Combining Eqs. 5 and 6, it is found that:

$$
\sqrt{I_\gamma(Q \rightarrow 0)/n_p} \approx -\rho_{\text{sol}}^d(\gamma)L(n_p)\sqrt{S_{SR}(Q \rightarrow 0)} + b_{\text{polymer}}\sqrt{S_{SR}(Q \rightarrow 0)}, \quad (7)
$$

where $L(n_p) = v_{\text{polymer}} + v_{\text{cavity}}(n_p) v_{\text{sol}} h(n_p)$. By measuring the samples with different $\gamma$ and plotting $\sqrt{I_\gamma(Q \rightarrow 0)/n_p}$ as a function of $\rho_{\text{sol}}^d(\gamma)$, $S_{SR}(Q \rightarrow 0)$ can be obtained from the vertical intercept. Figure 2 illustrates this method. The experimentally determined $S_{SR}(Q \rightarrow 0)$ for the measured concentrations, from low to high, are 0.665, 0.235, 0.143, 0.0877, 0.0388 and 0.0184, which correspond to $\phi_{HS}=0.05, 0.17, 0.23, 0.29, 0.40$ and 0.48, calculated with Percus-Yevick approximation [38] and Verlet-Weis correction [7, 39].

![FIG. 2. Illustration of the contrast-variation SANS method for the determination of $S_{SR}(Q \rightarrow 0)$. In this study, we prepared 4 solvents at $\gamma = 40\%$, 50\%, 65\% and 80\% for each $n_p$. 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.](image)

The Neutron Spin Echo (NSE) spectrometer provides a temporal range for the short-time diffusion of colloidal suspensions [33]. We measured the star polymeric dispersions with NSE at $Q = 0.04$ Å$^{-1}$ to determine $D^{(SS)}$. This $Q$ value is much smaller than $2\pi/R_g^d$ ($R_g^d = 19$ Å is the radius of gyration of an isolated star) so that the dynamical contribution of rotational diffusion and intramolecular motion are much less than that of the translational diffusion and therefore can be reasonably ignored. In order 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. The $D^{(LS)}$ was measured with the diffusion Nuclear Magnetic Resonance (NMR) spectroscopy. Both the measured results of $D^{(SS)}$ and $D^{(LS)}$ are shown in Fig. 3 [39]. It is seen that, as $c$ increases, $D^{(LS)}$ decreases faster than $D^{(SS)}$.

![FIG. 3. The measured short-time and long-time self-diffusion coefficients of the star polymer dispersions as a function of concentration.](image)

Knowing $D^{(SS)}$, $D^{(LS)}$ and $\phi_{HS}$, we are able to check the predicted dynamic equivalence in colloidal dynamics. In Fig. 4 (a), we plot the reciprocal of the dimensionless long-time self-diffusion coefficient, defined as $D^* = D^{(LS)}/D^{(SS)}$, as a function of $\phi_{HS}$. An excellent agreement between the experimental result and the HS prediction is seen. Since the interparticle interaction of star polymers is very soft and $c$-dependent, this observation supports the softness- or potential-independent nature of the dynamic equivalence. We also calculate the “apparent volume fraction” of the star polymer with $\phi' = \frac{4}{3}\pi R_g^3 n_p$ and present the result in the inset of Fig. 4. In this definition, the effect of particle interpenetration and deformation are disregarded. As seen, the experimental points systematically deviate from the HS prediction. In Fig. 4 (b) we plot the effective HS radius of a star $R_{HS}$ as a function of $\phi_{HS}$ ($\phi_{HS} = \frac{4}{3}\pi R_{HS}^3 n_p$). $R_{HS}$ starts decreasing at $c^* \sim 15$ wt.\% as $c$ increases. The decreasing of $R_{HS}$ makes the slowing of the dynamics of the star polymer dispersions a fragile behavior, which is HS-like [23]. $c^*$ corresponds to the threshold $c$ from where the peak of $I(Q)$ starts weakening, as shown in Fig. 1. Therefore, our method naturally finds the critical concentration that signifies the change of the interparticle interaction and the onset of the anomalous behavior in the $S(Q)$ of the soft colloids.

This study belongs to the scope of the dynamic universality, which claims the existence of universal characteristics in the dynamics of liquids [40–53]. Different scaling rules have been proposed, and many of them employ the HS system as a reference [10–19, 50–52]. Particularly,
FIG. 4. (a) The reduced long-time self-diffusion coefficient $D^*$ as a function of $\phi_{HS}$. The symbols represent the experimental result of the star polymer dispersion. The line represents the result of the HS colloidal liquid given by the SCGLE theory [18]. It is seen that the HS curve gives an excellent prediction to the behavior of the star polymer dispersion. The inset gives the result with a different method for determining the volume fraction of star polymer: $\phi' = \frac{4}{3} \pi R^3 g n_p$. (b) The effective HS radius of the star $R_{HS}$ as a function of $\phi_{HS}$.

Liu et al. show that the dynamics of liquids can be scaled with Temperature/Pressure at low pressure limit [51] [52]. Our result is consistent with this scenario due to the correspondence between pressure and $\chi_T$ or volume fraction at a constant temperature [51]. In addition, Dyre et al. [46-49] propose a concept of isomorph for liquids, which suggests that liquids have the same static and dynamic correlation functions if they are isomorphic. This scaling works perfectly for liquids with Inverse-Power-Law (IPL) potentials. Our result can be understood within this framework if we consider the HS interaction as an IPL potential with a large exponent [54].

The observed soft-hard dynamic equivalence, as well as previous theoretical and simulation results, suggests that the dynamics of liquids has a geometric nature of the average accommodation of N repulsive particles confined in a volume $V$. This excluded volume effect becomes more significant when the density or concentration is high. In this case, the packing of particles is so tight that the detail of the interparticle repulsion becomes less important. From this point of view, it is expected that for some potentials the dynamic scaling will fail. An example is the Gaussian-core potential that allows a complete overlap between particles [55]. Actually, it has been proved that dynamic universalities cannot work for this potential [59] [60]. Another example is the potential with a strong and short-ranged attraction. Solutions with this kind of potential exhibit clustering, which leads to unique dynamic features [57].

To summarize, the aim of this study is twofold: First of all, inspired by recent BD results [10], we propose a definition of $\phi_{HS}$ for SR liquids by employing the condition of compressibility equivalence, and present a model-independent method to extract $\phi_{HS}$ for soft colloids from SANS experiments. Secondly, by measuring star polymer dispersions, we experimentally verify that the slowing of the long-time colloidal dynamics, normalized by the short-time self-diffusion coefficient and scaled by $\phi_{HS}$, is equivalent to the HS behavior.

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