Surface Fluctuations Dominate the Slow Glassy Dynamics of Polymer-Grafted Colloid Assemblies

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ABSTRACT: Colloids grafted with a corona layer of polymers show glassy behavior that covers a wide range of fragilities, with this behavior being tunable through variations in grafting density and grafting chain length. We find that the corona roughness, which is maximized for long chain lengths and sparse grafting, is directly correlated to the concentration-dependence of the system relaxation time (fragility). Relatively rougher colloids result in stronger liquids because their rotational motions become orientationally correlated across the whole system even at low particle loadings leading to an essentially Arrhenius-like concentration-dependence of the relaxation times near the glass transition. The smoother colloids do not show as much orientational correlation except at higher densities leading to fragile behavior. We therefore propose that these materials are an ideal model to study the physical properties of the glass transition.

The physics of the glass transition is a long-standing unsolved problem. As a system goes through its glass transition, for instance as a result of a fast temperature or pressure quench, it typically retains its liquidlike structure, but its viscosity drastically increases until it finally freezes. Unfortunately, the factors governing the behavior of the viscosity near the glass transition, which is directly related to the system’s fragility, are still poorly understood. Fragility, which is typically defined as the slope of the relaxation time vs inverse temperature in the vicinity of the glass transition, is a measure of how quickly the relaxation time of the material diverges. Angell et al. have examined the viscosity of many glass-forming liquids and found that they can be separated into two main groups on the basis of their fragilities. One group is characterized by a viscosity that follows an Arrhenius behavior (strong liquid) and the other by a non-Arrhenius behavior (fragile liquid). These materials have low and high activation energies for the viscosity—temperature relationship, respectively, when approaching the glass transition. It is generally believed that materials with directionality in their intermolecular interactions, e.g., SiO₂, form strong liquids, whereas materials whose components interact through isotropic potentials typically form fragile liquids. Since it is hard to directly observe the local structure of molecular systems in the vicinity of the glass transition, it is thought that the larger sizes of colloidal glass formers make them much more facile for direct observation, e.g., using confocal microscopy. Most experiments with colloids have been performed on spherical particles, and have almost exclusively resulted in the formation of fragile liquids. Thus, these systems have not been particularly useful for systematically understanding the subtleties underlying the behavior of the viscosity across a range of different fragilities. Very recently researchers have found that microgels and star polymers showed strong liquid behavior, thus implying that the fragility was strongly related to particle softness. Note that this kind of colloidal system is not completely equivalent to typical glass-forming-liquids; in the latter case decreasing temperature leads to the slowing down of kinetics, resulting in vitrification. On the other hand, in colloidal systems, compression (or increasing concentration) leads to vitrification. Therefore, by analogy to typical glass formers, we define a pseudofragility by replacing temperature with concentration in determining the slope of the relaxation time curve when approaching the glass transition (see eq 2 below and associated discussion).

Here we reiterate that the physical picture about (i) how softness determines fragility and (ii) whether the concept of softness could be applied across a range of systems, are still open questions. To address these issues, we have studied the glassy behavior of colloids grafted with polymer chains (hairy colloids, HCs) using computer simulations and show that they can cover the full range of fragility with the roughness of colloids, which is related to softness, apparently dictating behavior. One of the key features of these colloids is that, at low grafting densities, fluctuations of the grafted chains result in significant degrees of colloidal shape anisotropy. We use numerical simulations to characterize these effective shapes for a range of parameters (grafting chain length and grafting density dependence of the system relaxation time (fragility). Relatively rougher colloids result in stronger liquids because their rotational motions become orientationally correlated across the whole system even at low particle loadings leading to an essentially Arrhenius-like concentration-dependence of the relaxation times near the glass transition. The smoother colloids do not show as much orientational correlation except at higher densities leading to fragile behavior. We therefore propose that these materials are an ideal model to study the physical properties of the glass transition.

Received: June 4, 2018
Published: August 27, 2018
density) and study their role on the dynamics of the system at different volume fractions. Remarkably, we find that the degree of anisotropy of the colloids, which we characterize in terms of their surface roughness, is directly related to the fragility of the resulting glass formers. Our numerical results also suggest a simple physical picture of how fragility may be related to the emergent microscopic interactions between the colloids.

The system under investigation consists of purely repulsive Weeks–Chandler–Andersen spherical particles onto which we randomly graft polymer chains of equal length (the chains are modeled with a standard bead–spring representation). Note that we simulate systems with no solvent; this is in the spirit of recent experiments where polymer-grafted nanoparticles are used to construct a novel class of one-component nanocomposites.\textsuperscript{14,15} The static and dynamic properties of HCs are investigated using molecular dynamics simulations (for details on the calculations and the model, we refer the reader to the Methods section).

Figure 1 illustrates the averaged structure of an HC. Figure 1a shows how the effective corona coverage of an HC varies with the length and density of the polymers grafted on its surface. The thickness of the corona at each point on the colloid surface is constructed by finding all the monomers intersecting with a radial vector (within a small range of solid angle) connecting the center of the colloid to the point of interest in its surface, and selecting the farthest monomer along this vector. This radial distance is averaged over many uncorrelated configurations, and is calculated on \( n = 4112 \) points homogeneously distributed over the colloid surface. We thus create a surface envelope around the colloid, which we term as the average corona surface. While the shape anisotropy can in principle be monitored using the radius of gyration tensor of these HCs, we expect that our more local representation will pick up corona density distributions in more detail. To further characterize these density distributions on the corona surface, we use its roughness

\[
R_{\text{eff}} = h_{\text{ave}} + R_c, \quad \text{where} \quad R_c \quad \text{is the colloidal radius, which is set to} \quad 2.5\sigma, \quad R_{\text{eff}} \quad \text{increases monotonically with increasing} \quad f, \quad \text{(Figure 1b).}
\]

Figure 1c, shows how \( R_{\varphi} \), normalized by the colloidal radius \( R_c \), depends on the number of grafted polymers for different chain lengths, \( N_p \). Clearly \( R_{\varphi} \) is small across the range of surface grafting coverage when the chains contain just a few monomers, and \( R_{\varphi} \) tends to zero in the limit of large grafting densities; this is the isotropic brush limit. The largest roughness is typically achieved for long chains and sparse grafting. Most of the results discussed in this paper refer to this relatively sparse surface coverage.

We now turn to the discussion of HC dynamics at volume fraction \( \phi \equiv 4\pi N R_{\text{eff}}^2/3L^3 \). Here \( N \) is the number of HCs, and \( L \) is the side length of the cubic simulation box. Figure 2a

\[
\phi \text{-dependence of configuration parameters of HC. Red: } (f = 20, N_c = 30), \quad \text{Orange: } (f = 20, N_c = 20), \quad \text{Green: } (f = 20, N_c = 10), \quad \text{Blue: } (f = 10, N_c = 5), \quad \text{Purple: } (f = 5, N_c = 5). (a) \text{Effective average radius, } R_{\text{eff}}/R_c, \quad \text{and (b) Average roughness, } R_{\varphi}/R_c. \quad \text{Softness is defined as } dR_{\text{eff}}/d\phi.
\]

shows how \( R_{\text{eff}} \) and \( R_{\varphi} \) depend of \( \phi \), respectively. Clearly, both \( R_{\text{eff}} \) and \( R_{\varphi} \) decrease monotonically with increasing \( \phi \), a tendency strongly dependent on \( f \) and \( N \). Here we define the HC softness as \( dR_{\text{eff}}/d\phi \).

The self-part of the intermediate scattering function (ISF) associated with the motion of the center of mass of a colloid (Figures 3) is defined as follows:

\[
\text{Figure 1. Configuration of HCs. (a) Corona structures of hairy colloids. The color gradients are related to the thickness of corona, } h_i/R_c. \quad \text{Red is the colloid surface. The diameter of the colloid, } 2R_c, \quad \text{and that of the polymer beads are set to } 5.0\sigma \text{ and } 1.0\sigma, \quad \text{respectively. (b) Effective average radius, } R_{\text{eff}}/R_c, \quad \text{as a function of the number of grafted polymers for several different chain lengths. (c) The average roughness, } R_{\varphi}/R_c, \quad \text{as a function of number of grafted polymers for a range of chain lengths.}
\]
\[ E_i(q, t) = \frac{1}{N} \sum_{k} e^{i(q(l(t) - r(0))} \]  

Figure 3. Translational dynamics of HCs. Plots of the self-intermediate scattering function (ISF) as a function of time for particles with: (a) large roughness \((f = 20, N_p = 30, R_g/R_s = 1.12)\), and (b) small roughness \((f = 5, N_p = 5, R_g/R_s = 0.135)\). Lines are fits to the Kohlrausch–Williams–Watts function. (c) and (d) illustrate the \(\phi\)-dependence of the stretching parameter, \(\beta\) for particles with: (c) large roughness \((f = 20, N_p = 30, R_g/R_s = 1.12)\), and (d) small roughness \((f = 5, N_p = 5, R_g/R_s = 0.135)\).

\[ \tau_i(\phi) = \tau_{i,0} e^{D \phi / (\phi_0 - \phi)} \]  

Here, \(\tau_{i,0}\) is the relaxation time in the dilute limit, \(\phi_0\) is the extrapolated volume fraction at which the relaxation time is predicted to diverge, and \(D\) is the fragility index, which effectively quantifies the sensitivity of the colloidal dynamics to volume fraction changes.

The “activation energy” associated with the dynamics of a fragile liquid is expected to have a significant dependence on \(\phi\), whereas for a strong liquid it does not. Typically, for strong liquids \(\phi_0 \gg \phi_g\), the “glass transition” volume fraction defined by \(\tau_g(\phi_g)/\tau_{i,0} \approx 10^6\), and thus \(\tau_i \propto e^{D \phi / (\phi_0 - \phi)} \propto e^{D \phi / \phi_g}.\)

One would thus expect Arrhenius-type behavior, with \(E \approx D \phi_g\) playing the role of the “activation energy.”\(^1\) Figure 4a and Figure 4b show that the \(\phi\)-dependence of \(\tau_i\) can be fitted using the VFT functional form. Crucially, \(\tau_i\) shows a strong dependence on polymer length and grafting density, and we find a remarkably simple linear relation between the fragility \(D\) and the colloidal roughness \(R_g\) (Figure 4c). We linearly extrapolate our data to determine that the fragility index of the uncoated colloid \((R_g \rightarrow 0)\) is \(D \approx 0.50\), which is compatible with fragility values reported for conventional colloidal glasses.\(^7,21\) When the roughness becomes of the order of the colloidal radius \((R_g/R_s \approx 1)\), we find a fragility index that is 20 times larger, i.e., \(D \approx 10\), which is compatible with values reported for strong liquids such as two-component network-forming liquids developed to mimic the behavior of SiO\(_2\).\(^22,23\)

Thus, depending on the polymer coating of the colloids, this simple system is able to span a wide range of fragilities. We also find that the softness \((dR_g/df)\) is linearly correlated with the fragility as reported in the literature (Figure 4d). However, if we extrapolate \(D\) as a function of the softness to the zero-softness limit, then we predict that \(D \approx 1.56\), which is much larger than the fragility of conventional hard colloids. Thus, we argue that softness alone is not sufficient to understand the fragility of these materials.

Usually, in strong liquids, the dynamics is determined rather locally. In a system with directional bonding as SiO\(_2\) or spin liquids,\(^24\) the dynamics is governed by the energy barrier associated with directional bonding. Before the bond breaking time, rotational motion does not occur. The scenario is quite different for fragile liquids, where particles need to move coherently over a mesoscopic length. These differences in particle dynamics should be reflected in the stretching parameter, \(\beta\). Hence we show the \(\phi\)-dependence of \(\beta\) for fragile and strong liquids in Figure 4c and Figure 4d. As reported many times in the literature, \(\beta\) decreases with increasing \(\phi\) and becomes constant \((\approx 0.6)\), which is in good agreement with experimental values and the theoretical estimate, \(3/5 = 0.6\), from the trapping model\(^25\) when approaching \(\phi_g\) for \(R_g/R_s = 0.15\) (fragile liquid, Figure 3d), while \(\beta\) is higher than 0.6, \(\approx 0.8\) for \(R_g/R_s = 1.12\) (strong liquid, Figure 3c), which is in good agreement with \(\beta\) reported for soft microgels.\(^9\) We also found a strong correlation between \(\beta\) and...
roughness/fragility (Figure 5a and Figure 5b). Interestingly, while \( \beta \) is almost constant for \( R_c/R_e \leq 0.5 \), it increases

monotonically with increase of roughness/fragility for \( R_c/R_e \gtrsim 0.5 \). Tanaka and his co-workers have proposed that the origin of fragility, especially for fragile liquids, is linked to the degree of frustration on crystallization.\(^7,^{21,24}\) Basically, roughness can be regarded as a disturbance for crystal order. For weak frustration, we expect crystal-like order to grow with volume fraction. This regime corresponds to \( R_c/R_e \gtrsim 0.5 \), local crystal-like ordering is hindered, and then a different scenario appears. Therefore, we further examine this large roughness regime below.

The strong correlation between the roughness of the corona surface and the fragility index of the resulting glass suggests that the effective HC–HC interactions have a significant degree of anisotropy. At large roughness we propose that this leads to strong correlations between the translational and rotational motion of the HCs. To verify this hypothesis, we examine the rotational behavior of the colloids for different concentrations and particle roughness by measuring the rotational correlation function:\(^2\)

\[
C^{(2)}_r(t) = \frac{1}{N} \sum_i \left\{ \frac{3\mathbf{u}_i(t) \cdot \mathbf{u}_i(0) - 1}{2} \right\}
\]

(3)

where \( \mathbf{u}_i(t) \) is a unit vector between the center of the colloid and a selected grafted bead on each of the colloids. We define the relaxation time \( \tau_r \) as \( C^{(2)}_r(t = \tau_r) = 1/e \). We fit this function with the KWW function. Figure 6 shows the rotational correlation functions \( C^{(2)}_r(t) \) at different densities and for two values of the particle roughness as a function of the colloidal mean-square displacement (MSD) normalized by the square-collidal roughness \( \{R_c(\phi)\}^2 \). Interestingly, in the case of the rough colloids the correlation functions at different concentrations essentially overlap (Figure 6a), and the location of the inflection point corresponds approximately to an MSD \( t = \tau_{\text{mid}} \approx \{R_c(\phi)\}^2 \). This suggests that the rotational motion of these “rough” colloids is correlated with their translational motion, with \( R_c \), the roughness, setting the length scale over which this correlation manifests. This behavior is consistent with the emergence of effective directional interactions between the colloids with a range that extends up to the colloidal surface roughness. It should be noted that both rotational and translational relaxation times have an Arrhenius-type dependence, and we calculate an \( E \approx 9.59 \) for the rotational relaxation process (not shown), which is in good agreement with the \( E \approx 9.67 \) derived from translational relaxation in Figure 5a. This good agreement indicates that the rotational relaxation is intimately related to the overall relaxation processes in this case. This is not the case for particles with small roughness (Figure 6b), for which the correlation between rotational and translational motion disappears. In other words, the few, large irregularities on the corona surface result in interlocking interactions between neighboring colloids. The \( \tau_r \) and \( \tau_{\text{mid}} \) do not track each other, and rotational relaxations are much slower than translational motions (Figure 6b). Interestingly, as the density of the system approaches the glass transition, \( \tau_r \) and \( \tau_{\text{mid}} \) approach each other, suggesting that translational motions are “catching up” to the slow rotations.

Figure 6c shows the ratio of \( \tau_r \) and \( \tau_{\text{mid}} \). Interestingly, in the case of large roughness, this ratio increases rapidly at low \( \phi \) and then becomes constant with increasing \( \phi \). This tendency strongly indicates that interlocking interactions are developing between neighboring colloids at low \( \phi \). In contrast, in the case of small roughness, the ratio of \( \tau_r \) and \( \tau_{\text{mid}} \) is almost constant in the dilute limit, but it drastically decreases just before \( \phi_g \). This means that strong decoupling of translational and rotational motion appears when approaching \( \phi_g \) in fragile liquids. Examples of this sort of behavior have been recently reported for many kinds of fragile liquids such as molecular liquids,\(^27,^{28}\) colloids,\(^21,^{29}\) and polymers.\(^30\)

If interlocking interactions develop between neighboring colloids, one would expect the formation of connected regions in the system with hindered rotational motion as one approaches the glass transition from below. To determine the degree of orientational persistence, we consider the function \( C^{(2)}_{ij}(t) \) between neighboring colloids, \( i \) and \( j \), defined as

\[
C^{(2)}_{ij}(t) = \frac{3 \cos^2 \{\theta_{ij}(t) - \theta_{ij}(0)\} - 1}{2}
\]

(4)
where $\theta_i(t)$ is the angle between $\vec{u}(t)$ and $\vec{u}_i(t)$, and colloids that are within a radius of $R_i + h_{\text{ave}}$ of each other are considered as neighbors. Any two neighboring colloids for which $C^p(r_{\text{max}}) \geq e^{-1}$ belong to the same cluster of spatially connected particles whose orientation persists over time. Figure 7a shows the average cluster size $N_d$ as a function of volume fraction $\phi$. In all systems, $N_d$ sharply increases above an onset volume fraction. We indicate the value of $\phi$ for which $N_d = N_i$, i.e., when all colloids are orientationally locked, as $\phi^*$. Remarkably, we find a linear relation (with a negative slope) between $\phi^*$ and $D$ as shown in Figure 7b; since $\phi_c$ shows the opposite dependence on $D$, this result implies that structural changes occur closer to the glass transition for more fragile materials. This can be intuitively understood by considering that in stronger liquids the colloids form a cluster with a rotational barrier due to roughness-induced interlocking, and hence the relaxation behavior is purely Arrhenius in the vicinity of $\phi_c$.

Interestingly, Mattsson et al., have reported that microgel particles consisting of interpenetrated and cross-linked polymer networks of poly(N-isopropylacrylamide) and poly(acrylic acid) can also be used to generate glasses with a wide range of fragility by adjusting the microgel softness. Several similar reports have appeared more recently. In the absence of a microscopic understanding of these systems, these results were understood by correlating the fragility with the elasticity of the deformable particles (which is directly related to the structure factor of the system). We clearly point to surface roughness as being a critical factor in determining fragility. It should be noted that while HCs can reproduce any degree of fragility, they cannot accurately describe the physical/chemical realities of various glass-forming liquids. In fact, while each glass-forming liquid has its own specific interactions between neighbors (e.g., strong energetic bonding in the case of SiO$_2$), HCs have exclusively entropy-driven (purely repulsive) interactions. Nevertheless, in this paper we show that their fragilities can be tuned from the fragile to the strong regime by simply varying the grafting parameters. Our claim is that HCs offer us the possibility to understand the kinetics of any kind of glass-forming liquids because of their unique ability to have a readily tunable fragility.

**METHODS**

**Simulation Model.** Grafted polymers are represented using the coarse-grained bead–spring model of Kremer and Grest. Each chain contains $N_p$ ($5, 10, 20, 30$) beads of mass $m = 1$. All beads interact via the Lennard-Jones (LJ) potential.

$$U_p(r) = \begin{cases} 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6, & r \leq r_c \\ 0, & r > r_c \end{cases}$$

Here, $r$ is the distance between two beads, $\epsilon$ is the Lennard-Jones unit of energy, and $\sigma$ is the bead diameter. $r_c = 2^{1/6} \sigma$. Beads along the chain are connected by an additional unbreakable finitely extensible nonlinear elastic (FENE) potential $U_{\text{FENE}}(r) = -\frac{1}{2}k \left( 1 - \frac{1}{\Delta^2} \right)$, with $\Delta = 1.5 \sigma$ and $k = 30 \epsilon/\sigma^2$. We use an expanded LJ interaction for pair interactions between colloid–colloid and colloid–polymer beads as follows:

$$U(r) = \begin{cases} 4\epsilon \left( \frac{\sigma}{r - \Delta} \right)^{12} - \left( \frac{\sigma}{r - \Delta} \right)^6, & r \leq r_c + \Delta \\ 0, & r > r_c + \Delta \end{cases}$$

We choose $\Delta = 4 \sigma$ and $\Delta = 2 \sigma$ for colloid–colloid and colloid–polymer bead interactions, respectively. $\Delta$ is the “shifted” distance which ensures that $U(r) = 0$ when colloid–colloid or a monomer–colloid are in contact. A colloid is represented by a uniform sphere of diameter $R_i = 2.5 \sigma$. One end monomer of the grafted polymer is fixed on the surface of the colloid (grafting point), $f(5, 10, 20, 30, 40, 50, 80)$ grafting points are then grafted on the surface randomly ensuring no overlap. Each of the $N$ ($216$) colloids have different patterns of grafting point arrangements.

**Molecular Dynamics Simulation.** All simulations are carried out using the LAMMPS parallel molecular dynamics (MD) package. NVT MD simulations are performed in a cubic simulation box. Temperature $T$ is set to $1.0 \epsilon/k_B$ and is maintained by a Langevin thermostat with a damping constant $\Gamma = 0.01 \sigma^{-3} (m/\epsilon)^{-1/2}$, $k_B$ is Boltzmann’s constant. The colloid positions are fixed in the single HC simulations, and only the dynamics of grafted polymers are enumerated so to observe corona configurations. The simulations are run for 1 million time steps, where each step is of length $dt = 0.005 \sqrt{m \sigma^2/\epsilon}$, to equilibrate the system and then another 100 million time steps for property calculations.

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**Author Contributions**

M.A. and S.K.K. designed the simulations. M.A. performed the computer simulations and analyzed the data. S.K.K. and A.C. supervised the project. The Article was written by M.A., A.C., and S.K.K. The project was conceived by M.A.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors thank Prof. Hajime Tanaka and Prof. Daan Frenkel for discussions and comments on this Article. This
work is financially supported by the National Science Foundation. S.K.K. acknowledges the National Science Foundation through Grant DMR-1629502. A.C. acknowledges the National Science Foundation through Grant DMR-1703873.

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