Diffusion Decoupling in Binary Colloidal Systems Observed with Contrast Variation Multispeckle Diffusing Wave Spectroscopy

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ABSTRACT: In the study of colloidal glasses, crystallization is often suppressed by leveraging size polydispersity, ranging from systems where particle sizes exhibit a continuous distribution to systems composed of particles of two or more distinct sizes. The effects of the disparities in size of the particles on the colloidal glass transition are not yet completely understood. Especially, the question of the existence of a decoupled glass transition between the large and small population remains. In order to measure colloidal dynamics on very long time scales and to disentangle the dynamics of the two populations, we employ contrast variation multispeckle diffusing wave spectroscopy. With this method, we aim to analyze the effect of size ratio, $a = r_{PS}/r_{NIPAM}$, on particle dynamics near the glass transition of a binary colloidal system. We find that both for long-time ($\alpha$-) and short-time ($\beta$-) relaxation, the dynamics of the small particles either completely decouple from the large ones ($a = 0.2$), moving freely through a glassy matrix, or are identical to the dynamics of the larger-sized population ($a = 0.37$ and 1.44). For a size ratio of 0.37, we find a single-glass transition for both particle populations. The postulated double-glass transition in simulations and theory is not observed.

INTRODUCTION

Glassy solids are an intriguing state of matter as even after decades of study, many questions are left open, such as the issues surrounding dynamic heterogeneities and the behavior of complex glassy mixtures. In general terms, the transition of a liquid into a solid is characterized by a distinct change in both the dynamical behavior of the system and its structural features. Although a liquid has an isotropic structure, the transition into a crystalline solid gives rise to a highly anisotropic structure with well-defined ordered positions for the constituent parts of the system, be they colloidal particles, molecules, or atoms. In the glass transition, a special case of liquid-to-solid transition, there is no appearance of an anisotropic and ordered structure. The system instead retains its isotropic and disordered structure, characteristic of the liquid phase, throughout the transition while particle dynamics slow down strongly. The lack of clear structural signs for the liquid–glass transition makes it elusive to investigate.

The dynamical slowdown that signals the glass transition often takes the form of a superexponential increase of the relaxation time of the sample with an increase in volume fraction, $\tau = \tau_0 \exp \left( \Delta \phi \phi_s \right)$ whose behavior is captured by the phenomenological Vogel–Fulcher–Tamann (VFT) equation: $\tau = \tau_0 \exp \left( \frac{\Delta \phi \phi_s}{\Delta \phi \phi_s - \phi_s^c} \right)$. More fundamental and accurate predictions have been made by mode-coupling theory (MCT), which has proved successful at predicting dynamics as systems approach their glass-transition. However, experimental deviations have been found to be close to the transition point.7,8

The experimental study of colloidal glasses is challenging because a system composed of colloidal particles of identical size tends to crystallize easily within experimental time scales, bypassing the metastable glass phase of interest. The quench rates needed to vitrify monodisperse non-hard sphere glasses have not been achieved in experiments.9 A common strategy to prevent a sample from crystallizing is to employ size polydispersity.10 Particles with an ensemble size polydispersity $>6\%$ are effectively prevented from crystallizing.10,11 The resulting large distribution of particle radii makes the analysis often more difficult. Therefore, experiments often use two distinct sizes instead of a continuous distribution,12 characterized by a size ratio of $a = r_{PS}/r_{NIPAM}$, where $r_s$ and $r_L$ are the radii of the small and large particle population, respectively. The ability of such a binary system to suppress crystallization depends on the size and mixing ratio. A particularly effective glass former is found at a 1:1 ratio of particles with $a$ between 0.7 and 0.8.13

In binary glasses, self-interactions—large–large and small–small—plus cross-interactions—small–large—are likely to give rise to complex size- and density-dependent dynamics. For example, the presence of polydispersity shows a marked effect on the vitrification behavior of a hard sphere system as extensive simulation work shown.14 In their hard sphere system with continuous polydispersity, the authors found decoupling between the larger- and smaller-sized parts of the particle population. To simplify the scenario, we explore the motion of a dilute phase of small “dopants” in a dense glassy
matrix of larger particles. Our systems are inspired by colloidal glasses but simplified as to remove some of the possible interactions and focus our research.

The small—small vitrification transition can have two distinct mechanisms depending on the doping degree of small particles in the matrix of larger particles. At high numbers of small particles, they are able to form an arrested phase by themselves when their local volume fraction crosses the glass transition, $\phi_s > \phi_c$. In contrast, at low numbers of small particles, the situation is more akin to a "doping" scenario. In this case, the phase of small particles can vitrify even when their volume fraction is below the glass transition, $\phi_s \ll \phi_c$. The small particles become increasingly confined in the interstitial space between large particles; this volume becomes ever smaller as the global volume fraction increases. As such, the small particles undergo dynamical arrest even when the total volume fraction of small spheres is much lower than the vitrification volume fraction. As a result of the simplification of interactions in our system, we are dealing with the second scenario in our experiments.

Even in systems with only two sizes and a relatively low presence of small particles, the "doping" scenario, complexity arises in the way the small trace particles interact with the matrix of large particles. For example, the structure of the matrix is crucial, as illustrated by the effect of a matrix that is attractive or repulsive with itself. Furthermore, the presence of small particles gives rise to depletion attractions dependent on their volume fraction, which complicates the phase diagram further.

Simulations and MCT predictions on the effects of binary mixtures on dynamical arrest show a decoupling in the dynamical behavior of large and small particles, giving rise to two distinct transitions: the larger species arrest at lower volume fraction indicated by the appearance of a finite localization length, whereas the smaller species retain a finite, though reduced, mobility. Evidence for this decoupling has also been observed in recent experiments using confocal microscopy on a polydisperse colloidal hard sphere system. So far, the effect of the size ratio between large and small particles on the predicted decoupling remains experimentally unexplored.

One of the large challenges to experimentally investigate the glassy phenomena is the inherently large range of time scales present in the dynamics of very dense systems. In dense suspensions, particles are effectively caged by their neighbors; it is the fast diffusive movement of particles within this cage, $\beta$-relaxation or "cage-rattling", that forms the fast dynamics. On much longer time scales, particles will escape this cage by means of $\alpha$-relaxation or "cage-breaking" and diffuse through the system. These two modes of motion give rise to the large range of time scales involved in the problem, often spanning many decades. This is only exacerbated by a possible decoupling between the dynamical behavior of the large and small population. The usual experimental techniques used to investigate colloidal glasses are either microscopy, especially confocal microscopy, or light-scattering techniques such as dynamic light scattering (DLS). Confocal microscopy offers the possibility to visualize and follow individual particles and thus also gives a means to discriminate between the two particle populations. However, microscopy is limited to a relatively small window of time scales which can be investigated; both fast time scales ($<10^{-3}$ s) and very long time scales ($>10^4$ s) are difficult to access because of the limited capture rate of cameras and the limit on storage space available for images. Light-scattering techniques are better suited to access the wide range of time scales. However, information about the distinct particle populations is not easily retrieved. An interesting merger between confocal microscopy and light-scattering methods can be found in the technique of differential dynamic microscopy (DDM), which has a lower wave vector range than DLS and can therefore probe larger length-scales. In this technique, dynamical behavior can be extracted from the intensity fluctuations of the difference between successive microscope images. DDM has been successfully applied to study hard sphere binary mixtures. However, DDM does come with a large data per-unit-time size and specialized analysis methods, making it less suitable to study dynamical behavior on very long times, as we intend to do.

In order to resolve these issues, we employ diffusing wave spectroscopy (DWS). This technique has been developed specifically to measure dynamical properties of samples that are so turbid that light will scatter many times in the sample before reaching the detector. In fact, the analysis is based on the assumption that photons scatter so many times that their path through the sample can be described as a diffusive walk. We specifically use a dual-detector variant of the DWS technique to extend our dynamic range to 7 decades in time. A single-photon avalanche photodiode (SPAD) and charge-coupled device (CCD) chip both detect the scattered light. The SPAD detector is used to detect correlations in the scattered light on very short time scales ($10^{-4}$ s $\leq \tau \leq 10^{-3}$ s), whereas the CCD chip, which provides as many detectors as there are pixels on the chip, can correlate scattered light on much longer time scales ($\tau \geq 10^3$ s).

Our search for a dynamical arrest transition in a binary system depends on our ability to measure the dynamics of the two populations separately. To do so, we use the method of contrast variation, where we selectively match the scattering contrast of one of the species in the system, thereby only measuring signal from the nonmatched species. The use of contrast variation is used as a method in neutron scattering and specific DLS methods where the interest lies with a polymer corona surrounding a refractive-index-matched particle.

To the best of our knowledge, this method has not been used to study the dynamics of individual particle populations in dense complex mixtures. We use poly(N-isopropylacrylamide) (pNIPAM) microgel particles as the refractive-index-matched matrix particles and polystyrene (PS) particles as the nonmatched probe particles whose size vary. pNIPAM microgel particles have an index of refraction very close to that of the aqueous medium, $n_w = 1.33$, as they are composed mainly of water ($\sim 95\%$), whereas that of PS particles differs a lot, $n_{PS} = 1.59$. Therefore, DWS will detect a weight-averaged signal heavily biased toward light scattered by the PS population; the contribution from the microgels is negligible.

By varying the size of the PS particles in the microgel matrix, we investigate the dynamics, over 7 decades in time, during the glass transition of binary mixtures at several size ratios, $a = n_{PS}/n_{pNIPAM}$. We find that the dynamics of binary mixtures is itself binary in nature: for a small size ratio, $a = 0.2$, the dynamics of the small particles are completely decoupled on all time scales from the larger microgel matrix, showing only hindered diffusion at long times scales. Intermediate to large size ratios, $a = 0.37$ and $a = 1.44$, show identical dynamics to
the microgel matrix. We observe no double-dynamical arrest at $a = 0.35$, where this was predicted to occur.18−21

# MATERIALS AND METHODS

**Particle Synthesis.** We synthesize pNIPAM particles with radius $r = 0.45 \mu m$ via an aqueous surfactant-free radical polymerization according to the method described in ref.33. We clean the particles using subsequent centrifugation, washing, and resuspension steps. After completing the cycle three times, we finally suspend the particles in 1 mM NaOH; this charges the acrylic acid functional groups in the microgels and swells the particle. In the case of pNIPAM particles, this swelling is known to be temperature dependent as the pNIPAM polymer has a lower critical solution temperature (LCST) around 37 °C.34 Indeed, we observe shrinking of the particles as the temperature changes from 15 to 45 °C. However, instead of a sharp transition at 37 °C, we find a gradual decrease over the entire temperature range (Figure 1). To get a sample of very high packing fraction, which we can dilute in further experiments, we centrifuge the microgels at 25 000g for 5 h. The volume fractions of a heavily diluted sample can be determined using an Ubbelohde capillary viscometer thermostatted at 20 °C. Via the Einstein relation, $\eta \equiv \frac{\eta_{\text{microgel}}}{\eta_{\text{water}}} = 1 + 2.5\phi$, we deduce the volume fraction of the dilute sample. We extrapolate the volume fraction from the dilute limit to higher concentrations. As the particle size may change because of osmotic deswelling, this leads to an apparent packing fraction $\zeta$.

With this technique, we find packing fractions of $\zeta = 1.12$ and $\zeta = 1.4$ for two prepared stock samples, from which we make dilutions. Note that we use the apparent packing fraction, $\zeta$, and not the true volume fraction, $\phi$. As the number density of particles increases and the osmotic pressure increases, the microgels tend to shrink in size. This effect makes the calculation of the real volume fraction very difficult; we use the linearly interpolated packing fraction $\zeta$ which ignores the shrinking effect at high densities.35,36

As scanning probe particles, we use PS particles with radii $r = 0.09 \mu m$, $r = 0.17 \mu m$, and $r = 0.65 \mu m$, prepared using emulsion polymerization according to the method described in ref 37, with the exception of the largest probe particles, which we synthesized using dispersion polymerization according to ref 38. The emulsion polymerization method gives us PS particles with polyNIPAM tails on the surface, which aids in minimizing the microgel−dopant interactions. We modify the dispersion polymerization slightly to also include the NIPAM monomer to achieve the same result. We clean the PS probe particles by repeated centrifugation and resuspension steps in a 1 mM NaCl solution. The three different combinations of the microgel matrix and one size of probe particles are diluted to a final PS volume fraction $\phi_{\text{PS}} = 0.01$ with a high microgel packing fraction $f_{\text{microgel}} > 1.0$.

**Contrast Variation MSDWS.** DWS Background. Disentangling the dynamics of individual species in mixed systems is challenging. The goal with those systems is to reliably measure data from both species separately. Much used optical methods, such as DLS, require the sample under study to be optically transparent such that the number of scattering events per photon is limited to 1. For dense systems, this is achieved by closely matching the refractive index of the system components and medium. Unfortunately, this method removes any contrast variation between the multiple species in the system and is therefore not useful to study complex mixtures. DWS, another optical scattering method to study dynamics, actually requires the sample to be turbid and to undergo multiple scattering.39 It is highly suited to study complex and dense mixtures, as we can eliminate the signal of single species by selectively matching their refractive index with the medium. As such, we gain access to the dynamical behavior of every single species in a mixture.

Our detectors measure light intensity over time, $I(t)$; from this, we calculate $g_1(t)$, the intensity autocorrelation function, using a hardware correlator. DWS theory is based on the field autocorrelation function $g_2(t)$, which we can obtain from $g_1(t)$ via the Siegert relation,

$$g_2(t) = \beta g_1(t) - 1.$$  

The exact data analysis methods used are described later in this section. Clearly, the resulting field autocorrelation function, $g_1(t)$, depends strongly on the system dynamics—our quantity of interest—and the probability distribution of possible photon paths in the sample, $P(s)$. In a general sense, this is captured by the central equation in DWS theory

$$g_2(t) = \int_0^\infty P(s) \exp \left( -\frac{2\tau}{\tau_s} \right) ds$$  

$$t/\tau = 6^{-1/2} \langle \Delta \tau^2(t) \rangle.$$  

This equation expresses the field autocorrelation function $g_1(t)$ in terms of the probe particle mean-squared displacement (MSD), $\langle \Delta \tau^2(t) \rangle$, by integrating over the contribution of every possible photon path length, $s$, to the decay of $g_1(t)$; here, $k_0 = 2\pi/\lambda$. Expressions for $P(s)$ can be derived on the basis of diffusion equations and the measuring geometry.40 For the case of noninteracting and purely diffusing particles in a transmission geometry, $P(s)$ is known and eq 2 becomes

$$g_2(t) = \frac{d}{d\tau} \frac{d}{d\tau} \left[ 1 + \frac{4}{3} \frac{\Delta \tau^2(t)}{\tau_s} \right].$$  

**Experimental Setup.** Measuring glasses requires methods with a large temporal dynamic range. We achieve this with a multispeckle DWS (MSDWS) setup, equipped with two detection pathways. This setup allows us to probe short time scales with a SPAPD detector and long time scales using a CCD camera.27

The setup uses a Cobolt Samba CW laser. The combination of a rotatable $\lambda$/2-plate and polarizing beam splitter cube (P-BGS) gives us fine control of the laser power used for the measurements. The measurement beam is expanded to a diameter of 15 mm, using a beam expander (Thorlabs BE10-532). The expanded beam is projected onto the sample in a cuvette with an optical path length $L = 5$ mm. We measure the transmitted scattered light after collimation with a long working distance 2X Mitutoyo objective. A nonpolarizing beam splitter cube splits the scattered light intensity 50:50 with one side leading to our SPAPD detector (Excites SPCM CD 3296 H) and the other toward a Fastec HiSpec 1 CCD camera−1280 x 1024 pixels. In front of both detectors is a polarization filter which eliminates scattered or few-times scattered light. The SPAPD detector has an internal pinhole ensuring that we only measure the signal from one speckle. The digital count rate signal from the SPAPD detector is correlated in time using a hardware correlator unit, ALV−7064/USB. A schematic overview of the setup can be found in Figure 2.

Two-Cell DWS. The dense-vitrified samples we measure are nonergodic. In the case of a nonergodic sample, taking an average over time is no longer equal to taking the ensemble average. Our SPAPD detector averages over time and thus does not gain a proper ensemble-averaged correlation curve, but one that is specific for the
It is the sample at several diameters of the diaphragm, between 1 and 5.5 mm. We select a diaphragm diameter controlled by the diameter of diaphragm to perform unwanted multispeckle averaging. The speckle size is possible, but if the speckle size becomes too small, each pixel may signal-to-noise ratio, we would like to image as many speckles as CCD chip, which can be approximated with the following relation:

$$\beta = \frac{1}{2} \ln \left( \frac{I_0}{I_{\text{ref}}} \right)$$

To maximize the CCD camera detection Signal-to-Noise Ratio.

Figure 3. (A) Probability distributions of $g_1(0)$ intercepts for different diameters, in mm, of diaphragm D2 as indicated by labels in graph. (B) Signal-to-noise ratio calculated as the average of the intercepts $g_1(0)$ divided by the spread of the intercepts $\Delta g_1(0)$, as a function of diaphragm diameter.

Figure 2. Schematic overview of our MSDWS setup with dual detection. We use a 1.5 W diode-pumped continuous wave (CW) solid-state laser with an emission wavelength $\lambda = 532$ nm. $\lambda/2$ half-$\lambda$ wave plate. P-BS polarizing beam-splitter cube. BD beam dump. M1 and M2 broadband mirrors. 10 x BE a 10 times beam expander, which in our case is made out of a single unit from Thorlabs, BE10-532. D1 and D2 adjustable diaphragms. S1 primary sample holder. O 2x infinity-corrected objective. NP-BS 50:50 nonpolarizing beam splitter cube. S2 secondary sample holder for an ergodic correction sample. A functional description of the setup can be found in the main text. P1 and P2 polarization filters.

Signal-to-Noise Ratio. To maximize the CCD camera detection signal-to-noise ratio, we would like to image as many speckles as possible, but if the speckle size becomes too small, each pixel may perform unwanted multispeckle averaging. The speckle size is controlled by the diameter of diaphragm D2 and its distance to the CCD chip, which can be approximated with the following relation:

$$s \approx \frac{d \lambda}{\alpha}$$

where $s$ is the speckle size, $d$ is the distance between the diaphragm and the chip which we set to 15 cm, and $\alpha$ is the diaphragm diameter.

We use the procedure outlined in ref 27 to optimize these settings. We measure $g_1(0)$ for 2500 distinct measurements of a PS in water sample at several diameters of the diaphragm, between 1 and 5.5 mm. We plot the distribution of intercepts and calculate its signal-to-noise ratio as $\langle g_1(0) \rangle / \Delta g_1(0)$ (Figure 3). On the basis of these measurements, we select a diaphragm diameter $a$ = 2.5 mm for all our subsequent measurements; this choice of diameter maximizes the signal-to-noise ratio while still having intercepts close to the theoretical value of $g_1(0) = 2$. We also observe intercepts higher than 2, which should theoretically not happen. As such, we do not take these values further into account.

Data Processing and Analysis. The data from the SPAPD is used to calculate $g_1(\tau) = 1$ with a hardware correlator. Via the Siegert relation, we arrive at the field autocorrelation function, $g_2(t)$, which we use for further analysis. Light measured by the CCD has passed through two sample cells. The measured signal $g_2^n(\tau)$ is composed of signals from both the primary and secondary cell; their relation is described by the following multiplication rule:

$$g_2^n(\tau) = (g_1^n(\tau))^2$$

From this relation, we get the primary correlation curve, $g_1^n(\tau)$, by dividing the measured signal by a correlation curve measured of only the secondary cell, $g_2^n(\tau)$, which we measure by simply removing the primary cell and keeping everything else as is with the exception of the laser power which we tune to appropriate levels for the secondary cell.

To analyze the CCD chip data (128 x 128 pixels from the middle of the chip), we treat every pixel as a separate light intensity detector and calculate the multispeckle-averaged $g_2^n(t_0)$ according to

$$g_2^n(t, t_0) = \langle I(t_0)^n I(t_0 + t_i)^n \rangle / \langle I(t_0)^n \rangle$$

where $I(t_0)$ is the light intensity measured at the start of the measurement on pixel $i$ and $I(t_0 + t_i)$ is the light intensity measured in $t$ s after the start of the measurement on pixel $i$. (...) indicates the averages over all pixels $i$ in the captured image. This multispeckle averaging allows us to measure without a second ergodic sample in the CCD chip light path.

To achieve the necessary temporal dynamic range, we need to combine the data from the SPAPD and CCD detectors. We truncate the data from the SPAPD at the point where our ergodic second cell starts to decorrelate (Figure 5). The data are truncated at 30 ms, which is far from the decorrelation time of the secondary cell but still offers an overlap with the CCD camera as the camera operates at a frequency of 500 Hz—with a minimal correlation time of 2 ms. Combining the data sets gives us an overlap region between 2 and 30 ms. To overlap the data, we scale the $\beta$ factor in the Siegert relation for the CCD data in such a way that we minimize the differences between the two data sets in the overlap region. For all samples, this gives us excellent agreement in the overlap region.

The quantity of interest is the characteristic decorrelation time, $\tau^a$. This value follows from fits to the combined $g_1^n(\tau)$ with the following expression, consisting of two stretched exponential decay functions:

$$g_1^n(\tau) = A \exp(\tau/\tau^a)^{-\alpha} - (1 - A) \exp(\tau/\tau^a)^{-\beta}$$

This functional form can fit both decays we expect: $\beta$-decay ($\tau^a$) and $\alpha$-decay ($\tau^a$). In the case of a sample with only one decay, we set $A$ to 1, eliminating the second term. After fitting, we need to correct $\tau^a$ for properties of both the sample under investigation and the measurement setup. The measured decay time of the sample is a function of both the photon transport mean-free path, $l^p$, and the optical path length, $L$, as $\tau = \tau^a/(l^p/L)^2$. We have no direct knowledge of $l^p$ for all our samples, but we are able to ascertain its value: the ratio between the photon transport mean-free path and the average light intensity is constant across samples. To exploit this, we measure a reference sample for which we do know $l^p$ without changing any experimental settings. As $I \propto l^p$, this allows us to calculate $l^p$ of our sample of interest via

$$l^p = \frac{l^p_i}{l^p_f}$$

where $l^p_i$ and $l^p_f$ are time-averaged intensities measured on the SPAPD detector for a sample of interest and the reference sample, respectively. All values for $l^p$ measured in this way fall between 0.08 and 0.16 mm (Figure 4).
RESULTS AND DISCUSSION

For all our samples we measure the correlation curve \( g_1(t) \) as a function of matrix packing fraction. We include the point \( \zeta = 0.0 \), which corresponds to a pure suspension of the probe particle without the presence of any microgel particles, thus measuring the Brownian time scale \( \tau_0 \).

The goal of our experiments is to shed light on the dynamical arrest of a binary-sized system, where the probe particles are dispersed in a matrix of refractive-index-matched pNIPAM microgels. To this end, we probe the dynamics of the system for three different-sized ratios and a range of packing fractions using MSDWS. We measure systems with size ratios \( a = \frac{\text{probe}}{\text{matrix}}, a = 1.44, a = 0.2, \) and \( a = 0.37 \). These correspond to the following three scenarios: at \( a = 1.44 \), the probe particles are larger than the matrix and are a direct measure for the dynamical behavior of the matrix; we expect the dynamical arrest of the tracers to effectively be a proxy for the behavior of the matrix particles. As we work at a low PS volume fraction, \( \phi = 0.01 \), the effects of probe–probe interactions are negligible. At a size ratio \( a = 0.2 \), the probe particles are very much smaller than the matrix; we would expect there to be two decoupled transitions. Finally, at intermediate size ratios, \( a = 0.37 \), we are left with an open question, do they display behavior in between the other two extremes or will they tend toward one of the limiting cases?

We start by measuring the field autocorrelation function \( g_1(t) \) for the large probe particles, \( a = 1.44 \) (Figure 6C). At lower packing fractions of the matrix, \( \zeta = 0.0, 0.14, 0.34, 0.69 \), and 0.76, we observe full and single decay of the correlation functions; the system is in a liquid state. As the packing fraction of the matrix increases, \( \zeta = 0.91, 0.92, 0.94, 0.95, 0.96, 1.0, 1.1, \) and 1.4, two decay modes become visible: a \( \beta \)-decay at short times due to cage-rattling and an \( \alpha \)-decay at longer times due to particles escaping from their cages. For the highest measured packing fraction, \( \zeta = 1.4 \), there is practically no decay of the correlation function inside the measurement window; at this packing fraction, the system is fully vitrified. From these curves, we extract the \( \alpha \)-decay times for the final decay by fitting to a double-stretched exponential function as described in the Materials and Methods section. We plot the resulting structural relaxation time, normalized to the decay time of the measurement at \( \zeta = 0.0 \), that is, the sample without any matrix particles present and corrected for \( \tau_0 \), \( \tau/\tau_0 \) as a function of \( \zeta \) (Figure 6D solid red circles). The superexponential increase in relaxation time as a function of packing fraction can be captured by the phenomenological VFT equation

\[
\frac{\tau}{\tau_0} = \exp \frac{A\zeta}{\zeta_0 - \zeta}
\]

This equation has seen success in empirically describing the vitrification behavior of many systems, ranging from colloids to molecular glasses, to metallic glasses.\(^5\) It captures our results well for \( A = 0.7 \) and \( \zeta_0 = 0.97 \), which implies that the system is fully vitrified close to the jamming point at \( \zeta = 1 \).

The observed distinction between \( \alpha \)- and \( \beta \)-relaxation originates in the MCT framework for the description of supercooled liquids. This framework operates with the internal assumption of ergodicity in the system under study; this is not the case for our samples at high packing fractions. Newer approaches have shed some light on the origin of the \( \beta \)-
the approximate displacement needed to achieve this amount characteristic decay times. While for the high size ratio, becomes immediately obvious with the plot of the extracted from the matrix. Even when fraction of the matrix, that is, they are dynamically decoupled thus only in concern a single species. we only measure the dynamical behavior of the probe species in our samples. Therefore it is difficult to link the observed decay modes to species of different sizes as the data only concerns a single species.

On the other end of the spectrum is the sample with size ratio $a = 0.2$. The correlation curves show a full decay even for matrix packing fractions higher than unity, where we now know that the matrix particles have vitrified. This difference becomes immediately obvious with the plot of the extracted characteristic decay times. While for the high size ratio, $\tau$ increases by 6 orders of magnitude, and for the small size ratio, only a very mild increase of approximately 1 decade is observed (Figure 6D). The dynamics of the small particles is thus only influenced very weakly by the increase in packing fraction of the matrix, that is, they are dynamically decoupled from the matrix. Even when $\zeta > 1.0$, we still find a full decorrelation. The weak increase is attributed to a shrinking pore size and thus increasing hydrodynamic coupling, as known for thermal motion in confinement.46,47

DWS in transmission mode is highly sensitive to even small displacements of the scatterers. From the central equation for transmission DWS (eq 1 in ref 25) and the fact that $g_r(t)$ will have decayed by a factor $1/e$ after a time $\tau(\ell^* / L)^2$, we can find the approximate displacement needed to achieve this amount of decorrelation, $\Delta r_{\text{rms}}$ via $^{45}$

$$\Delta r_{\text{rms}} = \frac{\sqrt{6} \cdot \ell^*}{k_0 \lambda}$$

(10)

$$k_0 = 2\pi/\lambda$$

(11)

For our systems, this evaluates to a displacement of $\Delta r \approx 13$ nm for $g_r(t)$ to decay by a factor 1/e. This displacement is small compared to the radius of the smallest probe particles, 90 nm.

It would be useful to know our particle sizes and their displacements relate to the interstitial voids as found in the glass formed by the large pNIPAM particles. As glasses are a highly irregular material, this calculation is not trivial. Therefore, we begin by considering a crystalline close-packed matrix at $\zeta = 0.74$, with which we can calculate the radius of the sphere, which fits in the interstitial spaces between the matrix particles. In the case of an fcc crystal, we find two distinct interstitial spaces, octahedral and tetrahedral spaces. They differentiate themselves by the number of particles surrounding such interstitial sites. The maximally allowed radius normalized by the radius of the base particles forming the crystal equals $r_{\text{max}} \approx 0.41 \cdot r_{\text{base}}$. In our case, $r_{\text{max}} \approx 450$ nm. With a radius of 90 nm, the smallest probe particles have ample space to move through the interstitial spaces. If we take into account the facts that at high packing fraction the microgels are likely to compress because of the increased osmotic pressure around them, and that our system is mostly not a fcc crystal but a disordered packing with, on average, larger interstitial sizes as they exist at lower volume fractions, it is no wonder that we observe full decorrelation for all matrix packing fractions with this specific size ratio.

The observed decoupling in the dynamics of the small probe particles and large matrix particles follows the prediction from MCT theory, simulations on binary amorphous systems, early experimental work, and spin glasses. Therefore, we would expect the small particles to undergo a localization transition as well at much higher matrix packing fractions. Unfortunately, the required packing fractions, $\zeta \gg 1.0$, were unattainable for this experiment. Instead of going to very high packing fractions, it should be possible to achieve the same effect by changing the size ratio under study to some intermediate value; with this approach, we do not change the pore sizes in the matrix but rather increase the size of the intruders. We expect the resulting effects to be the same.

For this intermediate size ratio, we use PS probe particles with a radius of 170 nm; with a resulting size ratio $a = 0.37$, the intermediate between 0.2 and 1.44 and below the critical values was calculated for an fcc crystal at $a < 0.41$. The correlation curves show the familiar two modal decays after the matrix packing fraction has increased above its point of dynamical freezing (Figure 6B). In fact, the resulting decay time follows, within experimental error, an identical dependence on $\zeta$ as the largest size ratio, $a = 1.44$ (Figure 6D, solid green triangles). From the correlation curves, we conclude that for our system, this intermediate size ratio behaves the same as the matrix itself; therefore, there is no decoupling in the dynamics of the two species.

Simulation work by Voigtmann and Horbach did find decoupled dynamics at a size ratio of 0.35, which contrasts our findings. Their simulations consisted of 2000 spheres, 1000 small particles and 1000 large particles, all interacting with a truncated Lennard-Jones potential such that only the repulsive part was taken into account. This Week—Chandler—Anderson...
potential approximates hard spheres with a small soft tail. To avoid crystallization, they used spheres with polydisperse radii. The fact that their system consisted of approximate hard spheres makes direct comparison with our work difficult. The matrix in our system is made of highly deformable and soft microgel particles, which can shrink and facet when needed in response to an increased osmotic pressure; the result of an increase in packing fraction. As matrix microgels shrink, because of osmotic deswelling, the effective size ratio will increase and a possible decoupling is suppressed. To fully answer the question whether there is an intermediate regime present where dynamics decouple at time scales in between the two extremes we have tested, an extensive size ratio series is required.

Although the correlation curves of the intermediate and large size ratios show an identical behavior in their relaxation time, this is not necessarily the case as regards the localization length of the particles trapped in their cages of matrix particles. The localization length, \( \delta \), is comparable to the size of the cage in which the probe particles are located at higher matrix packing fraction beyond their glass-transition point. We can access this length scale from the MSD of the particles; for glassy systems, the MSD has a plateau at intermediate time scales. This localization plateau is the square of a con-
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The full analytic result for the correlation function \( g_1(t) \) in transmission geometry is

\[
g_1(t) \approx \frac{k_0}{\sinh(k_0L\sqrt{\langle \Delta^2 \rangle /L^6})} \quad (12)
\]

with \( k_0 = 2\pi n/\lambda \). This gives us access to MSD curves directly from the DWS data after numerical inversion.

The smallest probe particles show the expected behavior in their MSD; at very low dilutions, their motion is purely diffusive with a slope of unity. As the packing fraction of the matrix increases, the dynamics slow down and become subdiffusive. This can be seen by the slope of the MSD curves on a log–log scale, which becomes <1 (Figure 7A). A full caging plateau, however, is never reached as was to be expected with a single-mode decay of \( g_1(t) \). For the intermediate and largest size ratios (Figure 7B, C), the situation is markedly different from the small probe particles, but similar between themselves. At low matrix packing fractions, there is again only diffusive movement of the probes. However, at higher packing fractions, we observe a caging plateau with an onset around \( t = 10^4 \) s. In these curves, the plateau is preceded by a region with a subdiffusive motion as the particle rattles around in its cage and it experiences hydrodynamic interactions with the cage “walls”. At long time scales, the plateau gives way to a new diffusive regime of \( \alpha \)-motion as particles escape from their cages and move around the sample.

From these curves, we can extract the localization length of the probe particles—the cage size experienced by these particles. To this end, we take the square root of the MSD value at a set time of 1418 s

\[
\delta = \sqrt{\langle \Delta^2 \rangle (t = 1418 \text{ s})}
\]

For both size ratios, which show caging plateaus, the trend of \( \delta \) with matrix \( \zeta \) follows the exact same trend. This leads us to conclude that not only are the two size ratios identical when it comes to relaxation times but that, unexpectedly, they feel similar cage dimensions as well. Thus, the glass transition is identical for these size ratios. This leads us to conclude that if there is indeed an intermediate regime where the probe particles experience a glass transition after the matrix particles, it should be found at a size ratio \( 0.20 < a < 0.37 \).

**CONCLUSIONS**

With extensive DWS experiments, we have tried to shed light on the dynamical behavior of binary-sized colloidal systems. We use contrast variation to probe the dynamics of a single species in the binary mixture. The base matrix consists of pNIPAM microgel spherical particles, which are doped with PS probe particles at several size ratios: \( a = 0.20, a = 0.37 \), and \( a = 1.44 \). With the largest size ratio, we essentially probe the dynamics of the microgel matrix and thus this gives us a baseline. We observe a clear dynamical decoupling between this large ratio and the smallest size ratio. Although the large probe particles exhibited the expected two-mode decay patterns of a glassy state, we observe no such decay patterns over a similar range in the matrix packing fraction. The small probe particles are able to move around in the interstitial spaces between the microgel matrix; their dynamical arrest will occur at microgel packing fractions, which we are unable to achieve in our experiments. This raises the question whether an intermediate state exists, where intermediate sized probe particles undergo dynamical arrest after the matrix but before the smallest probe particles. To this end, we measured samples at a size ratio \( a = 0.37 \), which lies between the largest size ratio and the smallest size ratio we have investigated. We have found no evidence for intermediate behavior as these particles followed the trends of the matrix, both in relaxation times in

**Figure 7.** Probe particle MSD, extracted from \( g_1(t) \) via eq 12. (A) MSD curves for a system with size ratio, \( a = 0.20 \) at the same packing fractions as shown in Figure 6A. (B) MSD curves for a system with size ratio, \( a = 0.37 \) at the same packing fractions as shown in Figure 6B. (C) MSD curves for a system with size ratio, \( a = 1.44 \) at the same packing fractions as shown in Figure 6C. (D) Localization lengths, \( \delta \), for every MSD curve that exhibits a plateau calculated as \( \sqrt{\langle \Delta^2 \rangle (t = 1418 \text{ s})} \), indicated by a solid vertical red line in panels B and C. Calculated for size ratio \( a = 0.37 \) (green triangles) and \( a = 1.44 \) (red circles). The dashed line is a guide to the eye. The diagonal solid line in panels A, B, and C is a line with a slope of 1.
$g_i(t)$ and in the localization length, $\delta$, experienced by the probe particles. The decoupling which we found at the most asymmetric size ratio has also recently been seen in systems consisting of hard spheres. The authors used experiments, simulations, and theoretical calculations to investigate their system. They also investigated the influence of the volume fraction of small particles, $\phi_s$, on the decoupling behavior and found that there is a transition volume fraction for this effect. We have done all our experiments at a constant and low-volume fraction of small particles; continued experimentation in our soft system with respect to the small particle volume fraction would certainly be interesting.

To gain full experimental understanding of the decoupling in dynamics and its features when it comes to the size ratio of a binary system, we need to extend our range of measured size ratios and volume fraction. It would be useful to remove the variability of the matrix; here, we used soft microgels which can swell and deform as needed. The use of an index-matched hard-sphere system would reduce this variability. A recently developed colloidal system, which can be index-matched and allowed for fine-tuning of the colloidal interactions playing a role by tuning the surface chemistry, would be an ideal candidate.

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Notes

The authors declare no competing financial interest.

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