Simulation study of Non-ergodicity Transitions: Gelation in Colloidal Systems with Short Range Attractions

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Computer simulations were used to study the gel transition occurring in colloidal systems with short range attractions. A colloid-polymer mixture was modelled and the results were compared with mode coupling theory expectations and with the results for other systems (hard spheres and Lennard Jones). The self-intermediate scattering function and the mean squared displacement were used as the main dynamical quantities. Two different colloid packing fractions have been studied. For the lower packing fraction, $\alpha$-scaling holds and the wave-vector analysis of the correlation function shows that gelation is a regular non-ergodicity transition within MCT. The leading mechanism for this novel non-ergodicity transition is identified as bond formation caused by the short range attraction. The time scale and diffusion coefficient also show qualitatively the expected behaviour, although different exponents are found for the power-law divergences of these two quantities. The non-Gaussian parameter was also studied and very large correction to Gaussian behaviour found. The system with higher colloid packing fraction shows indications of a nearby high-order singularity, causing $\alpha$-scaling to fail, but the general expectations for non-ergodicity transitions still hold.

I. INTRODUCTION

Colloidal suspensions are often referred to as model systems for studying fundamental problems in condensed matter physics [1]. Most of the properties of colloidal systems are similar to those of simple liquids, except for the difference in the time scales involved in the processes in liquids or colloids, making the latter more useful in the study of some basic questions. Moreover, the interaction forces between particles in a colloidal system are easily tailored (e.g. by adding salt or polymer). However, there are some features found only in colloids, such as aggregation or gelation, which makes the study of these systems even more fascinating.

Gel formation, or gelation, is found in systems with strong short-range attractions, and is a universal phenomenon observed experimentally in many different systems, ranging from colloid-polymer mixtures [2, 3] to charged systems [4] or to globular protein systems [5]. Gelation is the formation of a percolating network (typically fractal) of dense and more dilute regions of particles with voids which coarsen up to a certain size and freeze when the gel is formed. This process is observed in the structure factor as a low-$q$ scattering peak which moves to lower $q$, increasing its height, and then arrests [6, 7, 8]. Description of this phenomenon has been attempted with percolation theories, theories of phase separation for states inside the liquid-gas binodal (which is meta-stable with respect to fluid-solid coexistence for short interaction ranges) or in terms of a glass transition of cluster of particles [6, 9].

Recently, acknowledging its non-equilibrium character, gelation has been interpreted using the formalism of mode coupling theory, MCT, for non-ergodicity transitions [10, 11, 12]. This approach views the gel as particles trapped by a network of bonds which hinders the particle motion, resulting in a non-ergodic state. Thus, gelation is caused by formation of long lived bonds, whose collective arrest is described as a a normal non-ergodicity transition. (This is distinct from many earlier approaches whereby the bonds were assumed to form irreversibly from the outset.) In the present simulation study, we want to test this suggestion critically, thereby establishing the existence or otherwise of a non-ergodicity transition corresponding to bonding network formation.

Also present in colloidal systems is the equivalent of the usual glass transition in simple liquids, which occurs at high densities, and is driven by steric imprisonment. This transition has been studied experimentally and compared to MCT thoroughly [13, 14, 15, 16]. When two different non-ergodicity transitions are observed in a system, MCT predicts a high order singularity in the region where the driving mechanisms for both transitions are present [17, 18, 19]. Therefore, a higher order transition is expected at high attraction strength and high density in colloidal systems with attractive interactions [10, 20, 21].

Computer simulations have been used to test the expectations from MCT in many different systems, such as a Lennard-Jones liquid [22, 23, 24, 25], water [24, 27], strong glass formers [22, 23, 24] and polymers [28, 24, 29, 30]. The tests have shown that the predictions from MCT are correct, not only qualitatively but also, in part, quantitatively [33, 33]. However, they have also pointed out some differences, especially in the spatial correlations...
of particle mobility \[34, 37, 38, 39\]. In none of these simulated systems, however, did gelation occur, presumably because the attractions were not short-ranged enough.

In this work, we have used molecular dynamics simulations to study the properties of the gel transition, and compared them with the predictions from MCT. (This was initiated in \[40\] where some further results may be found.) We take the numerous universal predictions of the theory to test the scenario qualitatively. Comparing quantitative predictions available for systems of hard spheres \[11, 12\], spheres with short range attractions \[10, 13, 12, 21\], and the mentioned simulation studies, we identify the novel mechanism driving the non-ergodicity transition which is the cause of gelation for moderately dense suspensions. Molecular dynamics were used instead of Brownian dynamics because the choice of microscopic dynamics does not affect the relaxational dynamics of a system close to a non-ergodicity transition \[24\]. By means of the Asakura-Oosawa interaction potential \[43\], we simulate the behaviour of a colloidal-polymer mixture, which is a well-understood system \[14, 15, 14, 17\]. For short interaction ranges, this system exhibits a fluid-crystal transition, at intermediate densities and increasing attraction strength, with a liquid-gas transition metastable to the fluid-crystal one. In our simulations, the system was modified to prevent both of these phase transitions from occurring, in order to be able to study the transition from the fluid to the non-equilibrium states.

The paper is organized as follows: Section II describes some results from MCT which will be used in the subsequent analysis of the simulation results. In section III the simulation method is presented and the details are given. Section IV, deals with the results and is divided into four subsections studying i) the correlation function, ii) the time scale and the diffusion coefficient, iii) the mean squared displacement and iv) a higher colloid concentration. Finally, in section V, we present the conclusions of this work.

II. MODE COUPLING THEORY

In this section we will present the most important MCT results on non-ergodicity transitions and its self part, in terms of a fluctuating-force correlator \[18, 19\]. In this paper, only the self part of the density correlator will be studied, defined as:

$$\Phi_q^s(t) = \langle \exp \{i q (r_j(t) - r_j(0)) \} \rangle$$

where the brackets denote average over particle $j$ and time origin, and $q$ is the wave-vector. The equation of motion of $\Phi_q^s$ in Brownian (coarse grained) dynamics, is given by:

$$\tau_q \partial_t \Phi_q^s(t) + \Phi_q^s(t) + \int_0^t m_q(t - t') \partial_{t'} \Phi_q^s(t') dt' = 0$$

where $\tau_q$ is a single particle diffusive time scale and $m_q(t)$ is a mode coupling kernel which describes the cage effect \[50\]. Within MCT, glass states are given by non-zero solutions of this equation for the long time limit of $\Phi_q^s(t \to \infty) = f_q^s$, the so-called non-ergodicity parameter. It describes the glass structure and may also be called Lamb-Mössbauer factor. The glass transition is marked by a (generally) discontinuous transition from the unique trivial solution in the liquid, $f_q^s = 0$, to multiple solutions in the glass, $f_q^s > 0$, where only the highest solution is physical. Glass transitions can be classified according to the number, $l - 1$, of non-trivial solutions merging with the highest one, and the type of transition is noted as $A_l$.

For liquid states close to the glass, a two step decay is observed for the correlator; the plateau at $f_q^s$ and signals the proximity of the glass transition. Around this plateau, $\Phi_q^s$ shows some universal properties, depending on the type of transition. For the most common type of transition, $A_2$, the decay to the plateau, and that from the plateau, can both be expressed as power law expansions. In particular, the decay from the plateau is given by:

$$\Phi_q^s(t) = f_q^s - h_q^{(1)} (t/\tau)^\beta + h_q^{(2)} (t/\tau)^{2b} + O((t/\tau)^{3b}) \quad (3)$$

with $h_q^{(1)}$ and $h_q^{(2)}$ amplitudes and $\tau$ the final or $\alpha$-relaxation time scale. $b$ is known as the von Schweidler exponent, and depends on the details of the interaction potential. Expression (3) implies time scaling for the decay from the plateau, called $\alpha$-decay, for different states close to the glass transition. The time scale, $\tau$, diverges as the glass transition is approached according to a power law, with an exponent $\gamma$, which can be related to the von Schweidler exponent: $\tau \sim |\sigma|^{-\gamma}$, with $\sigma$ the distance to the transition \[11, 12\]. On the other hand, the wave-vector dependence of the non-ergodicity parameter and amplitudes gives some non-universal properties of the transition, providing information about the mechanism causing the non-ergodicity transition.

For high order singularities, the fluid states close by show again a two step decay in the correlation function, but the decays to and from the plateau are no longer power law expansions. Instead, logarithmic laws are obtained \[18, 19\]. A salient feature is that a logarithmic decay around the plateau is predicted:

$$\Phi_q^s(t) = f_q^{sA} - C_q \log (t/t_1) \quad (4)$$

where $f_q^{sA}$ is the non-ergodicity parameter of the high order singularity, $C_q$ is an amplitude and $t_1$ is a time scale (the time when the correlator lies on the plateau).

The mean squared displacement (MSD) can be studied instead of the correlation function, obtaining a similar two step behaviour. Similar asymptotic laws to describe the decay to and from the plateau can be derived, and the parameters and exponents can be related to those of the correlation function \[12\].
the MSD defines the localization length and is a measure of the size of the cage. However, it should be noticed that the cage, as formed by other particles, is constantly re-structuring cooperatively. Only when the particles have broken free of their cages, diffusive motion is observed, with a self-diffusion coefficient, \( D_s \), that tends to zero as the glass transition is approached as \( D_s \sim |\sigma|^\gamma \) for the usual A\(_2\) transitions.

Two different non-ergodicity transitions have been found in colloidal systems with a short range attraction [10, 21]: a steric hindrance driven glass transition and an attraction driven gel transition [10, 11, 12]. While the first is found at high densities and is qualitatively similar to the glass transition in the hard sphere system (HSS) or Lennard-Jones system (LJS), the gel transition occurs at high attraction strength for all volume fractions. Different properties for these two transitions are predicted, the main difference arising from the driving mechanism: the localization length is shorter in the gel than in the glass, resulting in higher non-ergodicity parameters. Also, a smaller von Schweidler exponent for the gel than for the glass is expected, implying a higher value of \( \gamma \), i.e. the transition as observed by \( \tau_q \) or \( D_s \) is more abrupt.

The actual shape of the non-ergodicity transition line depends on the details of the interaction potential, although some general features can be found. From lower to higher interaction strength, the glass line, is slanted to higher concentrations, showing that a weak attraction fluidizes the glass. However, at even higher interaction strengths, the gel transition occurs at lower colloid density than the higher attraction strength. As a result, a re-entrance transition is obtained at high colloid volume fractions. The line may be wedge-shaped or curved in this region, depending on the range of the interaction. If the line is wedge-shaped a high-order transition (generically A\(_3\)) is present near the corner, whereas none exists if the line is smoothly continuous. An A\(_3\) singularity appears right at the vanishing of the \( A_3 \) point when the line first becomes smooth [21].

### III. SIMULATION DETAILS

Equilibrium molecular dynamics simulations mimicking a colloid-polymer mixture were performed for a system composed of 1000 soft-core polydisperse colloidal particles. The core-core interaction between particles was modeled by:

\[
V_{sc}(r) = k_B T \left( \frac{r}{a_{12}} \right)^{-36}
\]

where \( a_{12} = a_1 + a_2 \), with \( a_1 \) and \( a_2 \) are the radii of the interacting particles. A flat distribution of radii with a width of \( \delta = 0.1a \), where \( a \) is the mean radius, was used. The exponent in \( V_{sc} \) was selected high enough to avoid problems related to the softness of the potential [5]. The polymer induces an attractive depletion interaction between the colloidal particles, which was modeled by the Asakura-Oosawa interaction potential [13]. The extension of this potential to take polydispersity into account reads [22]:

\[
V_{AO}(r) = -k_B T \phi_p \left\{ \left( \bar{\eta} + 1 \right)^3 - \frac{3r}{4\xi} \left( \bar{\eta} + 1 \right)^2 + \frac{r^3}{16\xi^3} \right\} + \frac{3\xi}{4r} (\eta_1 - \eta_2)^2 \left( \bar{\eta} + 1 - \frac{r}{2\xi} \right)^2
\]

for \( r \leq 2(a_{12} + \xi) \) and 0 for larger distances. Here, \( \eta_1 = a_i/\xi; \bar{\eta} = (\eta_1 + \eta_2)/2, \) and \( \phi_p \) is the volume fraction of the polymer. Note that the range of the potential is given by the polymer size, \( \xi \), and its strength by \( \phi_p \). This potential was modified around \( r = a_{12} \), to ensure that the minimum of the total potential \( V_{sc} + V_{AO} \) occurs at this point: for \( r \leq 2a_{12} + \xi/5 \) a parabolic form, which connects analytically to \( V_{AO} \) at \( 2a_{12} + \xi/5 \) and has a minimum in \( 2a_{12} \), was used. In our simulations, the range of the interaction, \( 2\xi \), was set to 0.2\( a \), which would correspond to polymers with \( R_g/a = 0.1 \) where \( R_g \) is the radius of gyration.

A long-range repulsive barrier was added to the interaction potential in order to prevent liquid-gas separation (as shown below). The barrier had a maximal height of \( 1k_BT \), according to a fourth-order polynomial:

\[
V_{bar}(r) = k_B T \left\{ \left( \frac{r - r_1}{r_0 - r_1} \right)^4 - 2 \left( \frac{r - r_1}{r_0 - r_1} \right)^2 + 1 \right\}
\]

for \( r_0 \leq r \leq r_1 \) and zero otherwise. The limits of the barrier were set to \( r_0 = 2(a_{12} + \xi) \), and \( r_1 = 4a \), which was enough to prevent phase separation. The maximum height of the barrier equals the depth of the depletion interaction at contact for \( \phi_p = 0.0625 \), much lower than the values where the gel transition takes place. The resulting total interaction potential, \( V_{tot} = V_{sc} + V_{AO} + V_{bar} \), is analytical everywhere. It is shown in figure 1, where in order to indicate the spread induced by polydispersity, the potentials among three different pairs with differing radii are plotted.

In our simulations, lengths were measured in units of the mean radius, \( a \), and time in units of \( \sqrt{4a^2/3v^2} \), where the thermal velocity \( v \) was set to \( \sqrt{3/4} \). Equations of motion were integrated using the velocity-Verlet algorithm, in the canonical ensemble (constant NTV), to mimick the colloidal dynamics. Every \( n_t \) time steps, the velocity of the particles was re-scaled to assure constant temperature. No effect of \( n_t \) was observed for well equilibrated samples. The time step was set to 0.0025. Equilibration of the systems was tested by monitoring the total energy, and other order parameters (see below), and by measuring \( \Phi_q(t) \) and the MSD at different initial times. When the order parameters were constant and the \( \Phi_q(t) \) and
MSD curves showed no dependency on the initial time (ageing), the system was considered to be equilibrated.

The volume fraction of the colloidal particles, $\phi_c = \frac{4}{3} \pi a^3 \left(1 + \left(\frac{a}{\delta}\right)^2\right) n_c$, with $n_c$ the colloid number density, and the polymer volume fraction, $\phi_p$, were the control parameters used to identify the states in the phase diagram.

In order to explore the whole $\phi_p - \phi_c$ plane in search of the gel transition, phase transitions which forbid access (in equilibrium) to important parts of the plane must be prevented. Several order parameters were used to identify different kinds of ordering in our system and to monitor whether unwanted liquid-gas or fluid-crystal transitions were taking place. First, the onset of phase separation involving states of different density can be detected by dividing the system into $n^3$ boxes and measuring the density in every box. The ‘demixing’ order parameter is defined as the standard deviation of the distribution of densities:

$$\Psi_n = \sum_{k=0}^{n^3} (\rho_k - \bar{\rho})^2$$  \hspace{1cm} (8)

where $\rho_k$ is the density of particles in box $k$, and $\bar{\rho}$ is the mean density. This parameter is close to zero for an homogeneous system, and increases if it demixes into phases of different density. In our case, $n$ has been set to 4, implying 64 boxes, and a box edge of about $5a$ (depending on $\phi_c$). On the other hand, the orientational order parameter, $Q_6$, as defined by Steinhardt et al. 53, 54, signals the presence of an ordered phase, and is used to detect crystallization.

The phase diagram was probed using these parameters. In figure 2 the results are presented for a bare system (monodisperse and without the long-range barrier), a polydisperse system without the long-range barrier, and the final system with both polydispersity and barrier. In this figure, the colloid volume fraction is constant, $\phi_c = 0.40$, and the polymer concentration varies; an isochore is studied. The sudden increase in both $\Psi_4$ and $Q_6$ occurring at $\phi_p = 0.20$ for the bare system, signals the crystallization boundary, in accordance with Dijkstra et al. 17. Because of the short range of the potential, this system has no liquid phase; i.e. the liquid-gas coexistence is meta-stable with respect to the crystal-gas transition.

When polydispersity is introduced in the system, crystallization is prevented, as indicated by the constant trend of both parameters close to $\phi_p = 0.20$. However, as the system now does not crystallize, the liquid-gas transition can be reached upon increasing the strength of the interaction. This demixing is signalled by an increase in $\Psi_4$, not involving local ordering. In order to avoid this separation, the long-range barrier has been introduced in the interaction potential. The energy of a dense phase is raised, and demixing is thus energetically unfavourable. Figure 2 shows that liquid-gas separation is indeed inhibited by the repulsive barrier. Instead, individual voids of finite size are created in the system, causing a low-$q$ peak in the structure factor, $S(q)$, presented in Figure 2.

![FIG. 1: Total pair interaction potential $V_{tot}$ as function of the radial distance $r = |r_1 - r_2|$ for three different particle pairs; a pair of particles with minimal radii $a_1 = a_2 = a - \delta$, one with average radii $a_1 = a_2 = a$, and one with maximal $a_1 = a_2 = a + \delta$ (from left to right). The inset shows the enlarged region of the attractive minimum. Crosses mark where the parabolic minimum smoothly matches to eq. (3).](image1)

![FIG. 2: Demixing ($\Psi_4$) and orientational ($Q_6$) parameters for $\phi_c = 0.40$ and increasing polymer fraction, $\phi_p$, for different systems: monodisperse without long-range barrier (squares), polydisperse without barrier (circles), and polydisperse with long-range barrier (crosses).](image2)
IV. RESULTS AND DISCUSSION

This system has been previously shown to undergo both the glass and gel transitions as stated by MCT. It also exhibits a logarithmic decay in the correlation function at high colloid concentration, indicating a high-order singularity in that region [40]. In this section we will discuss the properties of the gel transition, and compare them with MCT and with those of the HSS and other systems, which are similar to the glass transition at high colloid concentration. We test for differences by comparing quantitatively the non-universal features of the transition, which will aid in the identification of the driving mechanism.

The gel line is predicted to extend to low packing fractions with the same qualitative properties. In order to test these properties we have performed simulations at two different colloid concentrations, \( \phi_c = 0.40 \) and \( \phi_c = 0.50 \), where the gel line is far away from the percolation one. At high concentration, the higher order singularity is expected to affect the equilibrium states, disturbing some features of the gel transition.

A. Self-Intermediate Scattering Function

The scaling prediction for the \( \alpha \)-decay of states close to a non-ergodicity transition is tested in Figure 4 for constant colloid packing fraction, \( \phi_c = 0.40 \). Two different representative wave-vectors are presented in this Figure, \( q = 6.9 \) and \( q = 15 \). As observed at the glass transition in the HSS and many other different systems [22, 23, 27, 31, 34, 10], the \( \alpha \)-scaling property holds. In comparing these correlation functions with those typical for the HSS or LJS, it is noticed that in Figure 4 the \( \alpha \)-decay of the correlators is more stretched, implying a smaller von Schweidler exponent at the gel transition than at the glass transition. Because of this stretching in the \( \alpha \)-decay, a clear plateau is not observed, although a slowing down of more than four decades is studied. Nevertheless, extrapolating the relaxation curves to extract plateau values, much higher values are found than at the glass transition in the HSS or the LJS.

We have analyzed the state \( \phi_c = 0.40 \) and \( \phi_p = 0.42 \) in more detail, which shows four decades of slowing down compared to the purely repulsive situation upon turning on the attraction. Because scaling is observed in Figure 4, studying only one state is enough to analyse the \( \alpha \)-decay of the correlation function. The slowest state, \( \phi_p = 0.425 \) was not chosen because it strongly deviates from the expected behaviour of \( \tau_q \) vs. \( \phi_p \) (see Figure 8 and discussion thereafter). The correlation functions at different wave-vectors for state \( \phi_c = 0.40 \) and \( \phi_p = 0.42 \) are presented in Figure 5. The range of wave-vectors studied, where the plateau height changes is much wider than the range for a similar change in \( f_g \) at the glass transition of hard spheres or Lennard-Jones particles. This feature indicates that the relevant distances for the gel transition are much shorter than for the usual glass transition.

The correlation functions were measured until the average particle displacement was 5a, which is one fourth of the box size (21.95 a). Thus, extending this measurement to longer times in order to observe the whole \( \alpha \)-decay at low \( q \) is troublesome. If the diffusion coefficient diverges at the same rate as the \( \alpha \)-time scale (as predicted by
FIG. 4: Intermediate scattering function (self part), $\Phi_q^s$, vs. re-scaled time with the $\alpha$-time scale, $\tau_q$, for different states: $\phi_c = 0.40$ and $\phi_p = 0.375, 0.39, 0.40, 0.41, 0.415, 0.42$ and 0.425 from right to left. Two different wave-vectors are studied: $q = 6.9$ (upper panel) and $q = 15$ (lower panel), with the KWW fits (dashed line) included.

MCT), this problem would not appear. Thus, we are also observing a discrepancy between both time scale divergences, that will be further discussed below.

The impossibility of observing a clear plateau, as mentioned above, makes it more difficult to analyse the correlators, since $f_q^s$ cannot be fixed a priori. Therefore, the $\alpha$-decay of the correlation functions has been fitted using expression (3), with $f_q^s$, $h_q^{(1)}$ and $h_q^{(2)}$ as fitting parameters. The von Schweidler exponent was also fitted but was kept identical for different wave-vectors. It was found as $b = 0.37$, and the other results for the fitting parameters, are shown in Figure 6. The trends of these parameters are similar to that of the glass transitions in both HSS and LJS, but over a wider q-range in the gel case. This indicates that the localization length is quite different in the present system. The non-ergodicity parameter exhibits a bell shaped curve, whereas the first order amplitude describes a maximum. The latter is determined from the fit up to a prefactor which depends on the choice of $\tau$ in eq. (3). As an estimate we have used $\tau_q$ for $q = 9.9$ ($\tau_q$ is defined by $\Phi_q^s(\tau_q) = f_q/e$), which yields values that are similar (in magnitude) to the HSS. The second amplitude shows a monotonously increasing behaviour with $q$, in accordance with the HSS, but it is always positive, unlike the HSS where it goes through zero at the peak of $h_q^{(1)}$.

The non-ergodicity parameter, $f_q^s$, can be approximated using the Gaussian expression:

$$f_q^s \approx \exp \left\{ -q^2 r_l^2 / 6 \right\}$$

(9)

where $r_l$ is the localization length. This approximation is known to be valid for low wave-vectors, and important deviations from the Gaussian behaviour are expected close to the glass transition. However, the value for the localization length obtained from fitting this curve (solid line in Fig. 6), can be used as an estimate of the one in the MSD.
FIG. 7: Parameters used in the KWW fittings and comparison with the von Schweidler fitting. Main figure: $A_q$ (closed circles) and $f_q^s$ (open circles), $\beta_q$ (crosses) and $b$ (horizontal dashed line). Inset: $\tau^K_q$ (closed circles) and $\tau_q$ (open circles).

The localization length so obtained is $\tau^2_q = 0.0126 a^2$, much smaller than for the HSS or the LJS, where $\tau$ is of the order of the Lindemann distance. This feature shows that the process causing the non-ergodic transition in our case has a typical distance much smaller than in the case of glass transitions in the HSS or the LJS. This agrees with the observation and discussion about the height of the plateaus, and of the different q-range covered by $f_q^s$ in Figure 3. Whereas the glass transition in the HSS is driven by core-core repulsions, the gel transition is caused by the short range attraction, therefore by bonds between particles, (see inset to Figure 3) whose size is of the order of the interaction range. An interesting analogy has been established between the mechanisms driving the formation of gels and glasses, and the freezing transition.

The $\alpha$-decay of near-non-ergodic states can be also studied using the Kohlrausch-Williams-Watts (KWW) stretched exponential. The KWW expression is given by:

$$\phi^K_q(t) = A_q \exp \left\{ -\left( \frac{t}{\tau^K_q} \right)^{\beta_q} \right\}$$  \hspace{1cm} (10)

where $\beta_q$ is known as Kohlrausch exponent, which has been shown to coincide with the von Schweidler exponent at high wave-vectors. This expression has been fitted to very different systems, and describes the $\alpha$-decay down to zero. We have fitted this expression to the $\alpha$-decay in our system. However, since the correlators in Figure 8 do not show the complete $\alpha$-decay, we have fitted the expression to the master curve, obtained from the $\alpha$-rescaling. Two of these fittings are presented in Figure 8 by the dashed lines, showing that the KWW stretched exponential describes well the $\alpha$-decay in this system.

The fitting parameters, $A_q$, $\beta_q$ and $\tau_q$, are presented in Figure 8, and compared with the corresponding parameters in the von Schweidler formalism. In such a way, $A_q$ is compared with the non-ergodicity parameter, $\beta_q$ with the von Schweidler exponent, and the $\tau^K_q$ with $\tau_q$. As expected, the height of the plateau can be determined equally well both by the KWW or von Schweidler analysis. The same holds for the time scales, $\tau^K_q$ and $\tau_q$. The Kohlrausch exponent is expected to tend to 1 at low wave-vectors, and to approach the value of the von Schweidler exponent at high q. The low-q limit is explained because diffusion is the dominant process over long distances, whereas at short distances (comparable to the cage size) the dynamics is dominated by the cooperative local rearrangements. This behaviour is predicted from MCT, and has been observed in different systems, such as molecular glass formers, and in simulations of polymer melts, and of water.

In our case, the low-q limit is not observed, but $\beta$ rises as the wave-vector decreases, indicating that the expected behavior may appear at lower $q$ below the small angle peak in $S(q)$. At high wave-vector, the Kohlrausch exponent crosses the von Schweidler value, but stays close to it. Although an exact agreement is not observed, we may conclude that the correct general trend is obtained.

B. Time Scale and Diffusion Coefficient

An important universal prediction of MCT is the existence of power law divergences for both the time scale, $\tau$, and the inverse of the self diffusion coefficient $D_s$, with the same exponent in both cases, $\gamma$:

$$\tau_q \sim (\phi^G_p - \phi_p)^{-\gamma} \hspace{1cm} \text{and} \hspace{1cm} D_s \sim (\phi^G_p - \phi_p)^{\gamma}$$  \hspace{1cm} (11)

where $\phi^G_p$ is the polymer volume fraction where the gel transition occurs. The relation between exponent $\gamma$ and the von Schweidler exponent, $b$, is also universally established by MCT.

Testing of the power law divergence (and measuring of $\gamma$) is usually carried out plotting $\tau_q$ as a function of $\phi^G_p - \phi_p$ for different values of $\phi^G_p$, looking for a straight line. This method is cumbersome, even more as deviations from it are expected for states close to the transition, and precise values for $\gamma$ and $\phi^G_p$ cannot be given. To avoid this difficulty, we have calculated $\gamma$ from $b$, as given by MCT, and with this particular value of the exponent looked for the power law divergence. In such a way, we are testing the compatibility of MCT predictions with our data.

Figure 8 shows the wave-vector dependent time scale $\tau_q$ vs. $\phi^G_p - \phi_p$ for different wave-vectors. For every wave-vector, $\tau_q$ was extrapolated to zero, yielding a value for the polymer fraction at the gel transition, $\phi^G_p$. The final value of $\phi^G_p$, used in Figure 8, was calculated as the average value for all wave-vectors studied. The linear trends in Figure 8 for $\phi^G_p - \phi_p > 5 \cdot 10^{-3}$, shows the power-law behaviour predicted by MCT, with exponent $\gamma = 3.1$.
and $\phi^G_p = 0.4265$. The closest state to the gel transition, $\phi_p = 0.425$ deviates from the power-law behaviour observed for lower polymer fractions. Similar deviations have been observed in the HSS and LJS and can tentatively be attributed to thermally activated processes (or hopping events) [24].

As shown in eq. (11), MCT predicts a power-law for the self diffusion coefficient, $D_s$, with the same exponent as the divergence of the time scale. Simulations on HSS and LJS have shown that a power law divergence is indeed obtained, but with a different exponent than in the case of $\tau_q$. Using the same procedure as described above (calculating $\gamma$ from $b$ and extrapolating $D_s^{-1/\gamma}$ to obtain $\phi^G_p$) yields a value for $\phi^G_p = 0.4519$, with the same $\gamma$ as for the time scale. This value of $\phi^G_p$ is too far from that obtained using $\tau_q$. Therefore, we cannot have similar $\phi^G_p$ and $\gamma$ to explain the behaviour of both $\tau_q$ and $D_s$, implying that the MCT prediction, eq. (11) is violated.

In Figure 8 we present $D_s$ vs. $\phi^G_p - \phi_p$ using for $\phi^G_p$ both the value estimated from $\tau_q$ and that from $D_s$. We consider more desirable to have similar $\phi^G_p$ to explain the behaviour of both $\tau_q$ and $D_s$, even though this implies two different $\gamma$: $\gamma = 3.10$ for $\tau_q$ and $\gamma = 1.23$ for $D_s$. As obtained in other non-ergodicity transitions [22, 32, 34], the $\gamma$ exponent is lower in the diffusion coefficient than in the time scale, although the difference between both values of $\gamma$ is bigger in our case.

In order to stress the different $\gamma$ exponents in the divergence of the time scale and $1/D_s$, we have plotted $D_s\tau_q$ as a function of $\phi_p$ for different wave-vectors in the inset to figure 8. This product, that should be constant according to MCT, diverges as the polymer fraction approaches $\phi^G_p$. The divergence follows a power law with the exponent equal the difference between both values of $\gamma$.

The maximum in the self diffusion coefficient (upper-right corner of Figure 8) is a consequence of the re-entrant glass transition at high packing fractions [11, 22]. A weak short range attraction at first destabilizes the cage and thus the glass transition moves to higher particle concentration initially as the polymer fraction is increased. At constant colloid concentration the diffusion thus first speeds up with increasing $\phi_p$, until for intermediate attraction strengths the gel line is approached, where the opposite trend then dominates. At $\phi_p = 0.40$, the glass transition is rather far removed and thus has little effect, but the increase of $D$ is still measurable and the diffusion coefficient can be used as a measure of the distance to the closest transition. The maximum thus indicates the re-entrant shape of the non-ergodicity line.

The wave-vector dependence of the time scale $\tau_q$ can also be compared with theoretical predictions. At low $q$, the time scale is expected to behave as $q^{-2}$, corresponding to a diffusive process over large distances. Yet, because the simulated scattering functions exhibit non–exponential relaxation even for the smallest wave-vectors, this simple theoretical scenario is not expected to appear in our case. At intermediate wave-vectors, where the Kohlrausch exponent becomes comparable to the von Schweidler one the theory predicts a decrease as $q^{-1/b}$, whereas at even higher $q$, the distances involved are dominated by the microscopic dynamics, and corrections to this behaviour are expected [23]. The inset to Figure 9 shows $\tau_q$ for different states close to the gel transition. In order to make clear common properties the curves have been scaled vertically to collapse (main figure).

It can be seen in this figure that the behaviour of $\tau_q$ at low wave-vectors (below $q = 10$), indeed shows a $q^{-2}$ behavior, which however is not the one explained by MCT.
At higher $q$, another power-law trend is observed, with a higher exponent: $q^{-3.3}$. The crossover from the low-$q$ behaviour to the high-$q$ one, compares nicely with the wave-vector where the Kohlraush exponent becomes equal to the von Schweidler one (Figure 7). The exponent of the high-$q$ region yields $b = 0.30$, lower than the value obtained from the analysis in Figure 6. However, this value is quite close to the measured von Schweidler value and much smaller than the HSS one. Deviations from this power-law behaviour are observed at high $q$ for the lowest $\phi_p$ presented in the figure. These deviations are caused by the microscopic dynamics, as they occur when $\tau_q$ is lower than a certain value, regardless the polymer fraction. This value, presented in the inset as a horizontal line, is $t_0 \sim 0.6$, which agrees with the time one would estimate from the correlators in Figure 9.

## C. Mean Squared Displacement

We turn now our attention to the MSD curves, that were partially analysed to obtain the diffusion coefficients presented in Figure 4. We are only interested in the slowing down close to the gel transition and thus we do not show the MSD for low polymer fractions, where the attraction speeds up the dynamics and increases the diffusivity (see figure 9 and [11]). The MSD, after a short initial regime of free flight, $\delta r^2 \propto t^2$, slows down because of the particle interactions and takes longer and longer to reach the long-time regime diffusive, where $\delta r^2 = 6D _t t$. An important feature that can be obtained from the MSD of the particles in the system, is the localization length, where the particle interactions hinder particle motion most strongly, and in the idealized glass state, arrest it.

It can be compared with the estimate using the Gaussian approximation (see Fig. 1). In Figure 11 we present the MSD for increasing polymer volume fractions. As the gel transition is approached, the localization length shows up as an indication of a plateau, signaling the bond formation. As already discussed above, $\tau_1$ is much shorter than in the HSS glass transition (upper dashed line in Figure 1), because of the driving mechanism.

The lower dashed line in this figure is the localization length, as estimated from the non-ergodicity parameter using the Gaussian approximation ($r_1^2 = 0.0126$). Although a clear plateau has not fully developed in our curves, its height seems to be above that estimate, by a factor $\sim 1.5-2$. Since the Gaussian approximation works very well in the case of the HSS, this suggests big non-Gaussian corrections at the gel transition. Before testing the Gaussian approximation, we stress that the localization length gives a typical size of the mesh of bonds formed between neighbouring particles, and that the slow structural units are continuously and cooperatively rearranging. In order to test this idea about a correlated region which cooperatively rearranges with and around each particle, a single mobile particle is considered in a fixed environment. A well equilibrated system with $\phi_p = 0.425$ is frozen, and only one particle is allowed to move. This mobile particle now explores a fixed environment, providing the structural size of the region it is confined to. The mean squared displacement so obtained is given in Figure 11 (dotted line). Some particles (1.6%) were able to break their bonds and diffuse freely in the frozen environment. For the particles that stay localized, it can be observed that the length of the frozen bonds is much smaller than the localization length. This fact demonstrates that the structure of bonds, like the repul-
sive cage at the glass transition in the HSS or LJS, is
dynamic, and constantly rearranges cooperatively. This
collective restructuring of the system fluidizes it, and re-
stores ergodicity, which cannot occur in the frozen sys-
tem, where the particles are not able to diffuse even at
very long times.

We turn now back to the Gaussian approximation, and
its accuracy. Usually, this is tested by measuring the non-
Gaussian parameter, defined as:

\[
\alpha_2 = \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1
\]  

(12)

where the averages imply ensemble averaging. This pa-
parameter measures the deviation of the probability density
function for the single particle motion from Gaussian be-
aviour, and vanishes for diffusive motion. Special care
must be taken when performing the ensemble averages
in polydisperse systems, as pointed out in [64]. The non-
Gaussian parameter must be calculated for every particle
(the averages in the definition above thus implying time-
origin averaging only), and particle averaging is taken
on the values of \(\alpha_2\) (so long as long enough time inter-
vals are studied, each particle will sample the distribution
relevant to its own size in an ergodic fashion). The non-
Gaussian parameters for states with increasing \(\phi_p\) are
presented as a function of time in Figure [2]. At short
times \(\alpha_2\) tends to zero, since the system shows Gauss-
ian behaviour during its unhindered ballistic regime. At
long times, when the particles break free from their bonds
and hydrodynamic diffusion holds, \(\alpha_2\) again goes back
towards zero. At intermediate times, corresponding to the
plateaus in both the correlation function and the mean
squared displacement, \(\alpha_2\) grows, since the single particle
motion hindered by bonding is not Brownian. As a result,
\(\alpha_2\) shows a maximum, whose height and position grows
in time, because the particles take longer and longer to
break free and start diffusing.

The behaviour of the simulated \(\alpha_2\) obeys the general ex-
pectations [20, 32, 39], but important differences are ob-
erved in the comparison with the results for the HSS
or LJS. Whereas in those cases the height of the max-
imum for similar (or even higher) \(\alpha\)-relaxation times is
around 2, at the gel transition much higher values are
measured. Another interesting difference is the failure of
the short time scaling, observed both in the HSS and
LJS. Both effects can be rationalized considering that the
cage is indeed a network of bonds in the case of a
gel, rather than a cavity. The strength of these bonds
is given by the intensity of the interaction, and thus, it
is modified for different states, disabling the short time
collapse. Because the bonds are short ranged, they af-
fect the particle motion from very short times onward, so
that the particles feel the hindrance much longer in the
gel case.

It can be concluded that the non-Gaussian corrections
are very important in the gel transition. Therefore, the
localization length estimated from the non-ergodicity pa-
rameter may be inaccurate, as discussed above. However,
it still provides an indication of how small the localization
length is. A better indication of \(r_1\) can be obtained within
the Gaussian approximation if only low wave-vectors are
used in fitting expression (1). The fitted curve is pre-
sented in Figure [5] by the dashed line, where only the
three lowest \(q\)'s are fitted. The estimated \(f_q^s\) deviates
from the data at higher wave-vectors, showing high non-
Gaussian corrections. The localization length is higher
than the previous value: \(r_1^L = 0.0162\). Thus, this fitting
provides data more consistent with the MSD curves and
the non-Gaussian parameter.

**D. Higher Colloid Volume Fraction**

We move now to a higher colloid volume fraction:
\(\phi_c = 0.50\). These results are presented to supplement
the findings at the lower packing fraction and test for
the prediction of stronger stretching closer to the higher
order singularity. As indicated in the theoretical section,
MCT predicts a higher order singularity in the vicinity
of the junction of the gel and glass lines; i.e. at high
polymer and colloid densities. In this particular system
we found clear indications of this singularity in simul-
ations at \(\phi_c = 0.55\) and \(\phi_p = 0.375\) [41]. The isochore
under study now, \(\phi_c = 0.50\), could be close enough to the
higher order singularity to show some effects.

In Figure [13] we present the correlation functions for
increasing polymer fractions at the same wave-vectors as
Figure [1] re-scaled to collapse in the long-time decay. It is
interesting to note that the polymer concentrations stud-
ied in this case are lower than those studied at the lower
colloid volume fraction. In accordance with experiments
and theory, this indicates that the gel transition takes
place at lower polymer fractions the higher the colloid
concentration.

In Figure [13] it can be observed that the correlators

![FIG. 12: Non-Gaussian parameter \(\alpha_2\) as a function of time
for states approaching the gel transition at the same states as
Figure [4]. The maximum increases with increasing \(\phi_p\).](image)
Correlation functions for different polymer concentrations. From left to right: \( \phi = 0.35, 0.36, 0.375, 0.38, 0.385, 0.39 \). Two wave-vectors are studied, as labeled in the figures. The dashed lines represent the KWW fittings to the \( \phi = 0.40 \) correlation functions.

The similarity of both \( \alpha \)-decays was used in the von Schweidler analysis of the correlation function, and only the non-ergodicity parameter and amplitudes were fitted. Since the upper part of the decay is known to be affected by the higher order singularity close-by, that part must be discarded in the fittings. The correlation functions and fittings are presented in Figure 14 for the state \( \phi_c = 0.50 \) and \( \phi_p = 0.39 \), for the same wave-vectors as Figure 9. The main conclusion is that the late \( \alpha \)-decay at all wave-vectors can be correctly described by the von Schweidler decay, with the same exponent as the state at \( \phi_c = 0.40 \). The non-ergodicity parameters obtained from the fitting are slightly lower than those of \( \phi_c = 0.40 \), but similar within the error bars. According to MCT, \( f^* \) decreases when approaching the glass part of the non-ergodicity line (signalling an increase in the localization length). Our result is thus consistent with this prediction.

With these values of the non-ergodicity parameter one can define also the wave-vector dependent time scale, \( \tau_q \), as discussed above. In order to test the value of the von Schweidler exponent, using eq. (2) we have performed a three parameter fitting to obtain \( \gamma \) and \( \phi^G_p \). In Figure 14, \( \tau_q \) is presented as a function of \( \phi^G_p - \phi_p \) for different wave-vectors. The power-law fittings for two wave-vectors are also plotted and the critical polymer fraction \( \phi^G_c \) is given.

The values of \( \gamma \) obtained from this analysis for different wave-vector range from \( \gamma = 3.37 \) to \( \gamma = 3.82 \), the mean value being \( \gamma = 3.70 \). This value of \( \gamma \) implies a smaller von Schweidler exponent, \( b = 0.33 \), in disagreement with our previous estimate, but backing the MCT prediction. Using the same value of \( \phi^G_c \), the vanishing of the self-diffusion coefficient, \( D_s \), can be analysed, and is presented in the inset to this figure. A power-law is observed in this case, with an exponent, \( \gamma = 1.92 \), which, again in contradiction to MCT, leaves us with a big difference between the two values of \( \gamma \).

The diffusion coefficients in the inset of figure 14 again
likely grasp the re-entrant glass transition. They describe a maximum, more pronounced than that observed in Figure 9 because the glass line is closer to the $\phi_c = 0.50$ isochore. The minimum in $\tau_q$, which is observed only for $q = 3.9$, in an equivalent way indicates the shape of the non-ergodicity transition line. At higher wave-vectors, the glass transition causes very low $f_q^s$ and the time scales merge with the microscopic transient and thus this feature is suppressed.

The wave-vector dependence of $\tau_q$ can also be studied, as done for the lower concentration, yielding another estimate of $b$. In this case, a similar plot as Figure 14 is obtained, where the low $q$ region is compatible with a $q^{-2}$ behaviour, and a higher exponent at higher $q$, yielding a value of $b = 0.38$. This value is in agreement with the nice comparison between the $\phi_c = 0.40$ and $\phi_c = 0.50$ isochores, but not with $\gamma$ or the MCT prediction. We may then conclude that analysis of this state is extremely difficult, but our indications state that the von Schweidler exponent is similar for both packing fractions, but probably slightly lower in the higher concentration.

Finally, we would like to point out that the non-Gaussian parameter at this packing fraction shows a behaviour similar to that shown in Figure 12, i.e. the peak is as high, and no short-time scaling is observed.

V. CONCLUSIONS

In this paper, by means of simulations, we have tested the universal predictions of MCT for gelation in colloidal systems, viewed as an attraction-driven glass transition. The self parts of the intermediate scattering function for states close to this transition have been analysed and the results were compared with the theoretical predictions. For the $\phi_c = 0.40$ isochore, which is far enough from the high order singularity, the correlation functions can be $\alpha$-scaled. The time scale of the $\alpha$-decay was shown to obey a power law divergence, with an exponent, $\gamma$, related to the von Schweidler exponent, obtained from the early $\alpha$-decay. Both features are predicted by MCT for all non-ergodicity transitions. Also, the wave-vector analysis of the time scale follows the behaviours predicted by MCT, with a small difference in the value of the von Schweidler exponent.

The wave-vector analysis of the correlation functions depends on details of the interaction potential, and thus provides information about the mechanism, leading to the transition. In our case, it establishes that the gel transition is driven by a short-range mechanism, namely, bond formation, as observed in the pair distribution function. Additionally, it has been shown that the KWW stretched exponential can account for the $\alpha$-decay of the correlation functions, as in other non-ergodicity transitions.

We have also tested the Gaussian approximation, which works very well for the HSS. The non-Gaussian parameter, $\alpha_2$, establishes that this approximation is much worse in the case of the gel transition than for the glass transition. It was also tested when comparing the estimated localization length from the non-ergodicity parameter with the MSD of the particles. The diffusion coefficient has been also studied. It tends to zero as the transition is approached following a power-law, with an exponent much lower than $\gamma$, in accordance with simulations of glass transitions in other systems, but in disagreement with MCT, where both exponents are equal.

Finally, when the colloid concentration is increased, the system shows signatures of the high order singularity nearby and little can be discussed about the exponents $b$ or $\gamma$. However, only slight changes in the numbers are expected, since the qualitative behaviour is reproduced, except for the $\alpha$-scaling. Also, the diffusion coefficient follows a power law with a different exponent and the non-Gaussian parameter reaches values similar to the $\phi_c = 0.40$ case.

Therefore, our main conclusion is that MCT accounts for most features of the simulated systems on approach to the gel transition, but the discrepancies already found in other non-ergodicity transitions (such as the repulsion-driven glass transition in hard sphere systems) are also obtained here.

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