One-dimensional cluster growth and branching gels in colloidal systems with short-range depletion attraction and screened electrostatic repulsion

F. Sciortino,1 P. Tartaglia,2 and E. Zaccarelli1

1 Dipartimento di Fisica and INFM-CRS-SOFT,
Università di Roma La Sapienza, P.le A. Moro 2, 00185 Roma, Italy
2 Dipartimento di Fisica and INFM-CRS-SMC, Università di Roma La Sapienza, P.le A. Moro 2, 00185 Roma, Italy

We report extensive numerical simulations of a simple model for charged colloidal particles in suspension with small non-adsorbing polymers. The chosen effective one-component interaction potential is composed of a short-range attractive part complemented by a Yukawa repulsive tail. We focus on the case where the screening length is comparable to the particle radius. Under these conditions, at low temperature, particles locally cluster into quasi one-dimensional aggregates which, via a branching mechanism, form a macroscopic percolating gel structure. We discuss gel formation and contrast it with the case of longer screening lengths, for which previous studies have shown that arrest is driven by the approach to a Yukawa glass of spherical clusters. We compare our results with recent experimental work on charged colloidal suspensions [A. I. Campbell et al. cond-mat/0412108 Phys. Rev. Lett. in press].

Recent years have witnessed a progressive interest in the role of the inter-particle potential on controlling structure and dynamics of colloidal dispersions. Experiments,1 2, 6, 7, 8, 9, 10, 11, theory,12, 13, 14, and simulation15, 16, 17, 18, 19, 20, studies have provided evidence that when the hard-core repulsion is complemented simultaneously by a short range attraction (of finite depth) and by a screened electrostatic repulsion, particles tend to form aggregates, whose shape and size is sensitively dependent on the balance between attraction and repulsion.13, 21, 22, 23, 24. In some cases, the system shows an equilibrium cluster phase, where particles associate and dissociate reversibly into clusters.1, 4, 5. Interestingly enough, these cluster phases appear not only in colloidal systems but also in proteins solutions, in the limit of low salt concentration.13, 15, 16. Estimates of the ground state configuration of isolated clusters of different size19 suggest that, when the clusters diameter exceeds the screening length, the shape of the aggregates crosses from spherical to linear. Evidence has been reported that, for appropriate tuning of the external control parameters, colloidal cluster phases progressively evolve toward an arrested state.1, 4, 5, 10. It has been suggested, and supported by numerical simulations, that, in the case of relatively large screening length (i.e. the case of preferentially spherical clusters), dynamic arrest may proceed via a glass transition mechanism, where clusters, acting as super-particles interacting via a renormalized Yukawa potential, become confined by the repulsions created by their neighboring clusters.13. This mechanism is, in all respects, identical to the glass transition of Yukawa particles,25, 26, 27, 28, and leads, favored by the intrinsic polydispersity of the clusters induced by the growth process, to the realization of a Wigner glass. The simulation study13 showed that the resulting arrested state is not percolating, i.e. the arrest transition can not be interpreted in terms of the formation of a bonded network of particles.

A very recent experimental work10 has reported evidence of arrest via linear cluster growth followed by percolation, in a system of charged colloidal particles. In the studied system, the short-range attraction, induced via depletion mechanism, is complemented by an electrostatic repulsion, with a Debye screening length estimated of the order of $\xi/\sigma \approx 0.65$, where $\sigma$ indicates the hard core diameter of the colloidal particle. The quasi one-dimensional clusters observed via confocal microscopy are locally characterized by a Bernal spiral geometry,29, the same structure found as cluster ground state configuration for the case of screening lengths smaller than $\sigma$. The Bernal spiral, shown in Fig. 1, is composed of face sharing tetrahedra, in which each particle is connected to six neighbors.

![Bernal Spiral](image)

FIG. 1: A pictorial view of the Bernal spiral. Particles have been differently colored to highlight the presence of three strands. In this geometry, each particle has exactly six nearest neighbors.
colloids. In the first route, we control the attraction between colloidal particles via a temperature scale. In the second route — designed to make direct contact with the experimental work reported in Ref. \[10\] — we study an isothermal system where the repulsive part of the potential is fixed, while the attractive part of the potential is varied according to the concentration of depletant, to model the strength of the polymer-induced depletion interaction. We will refer to these two set of simulations respectively as temperature and polymer concentration route, naming them after the respective relevant control parameters.

We study — as a function of the packing fraction and of the attraction strength — the shape of the clusters (quantified via their fractal dimension), the local geometry around each particle, the inter-particle structure factor, the connectivity properties of the system. We complement the static picture with information on the inter-particle bond lifetime and on the dynamics of self and collective properties. We compare these quantities for particle bond lifetime and on the dynamics of self and collective properties. We compare these quantities for the two routes, and show that the two approaches provide a similar description of cluster growth, percolation and gel formation.

I. SIMULATION DETAILS

We study a system composed of \( N = 2500 \) colloidal particles of diameter \( \sigma \) and mass \( m \) in a cubic box of size \( L \), as a function of the packing fraction \( \phi_c = \frac{\pi \sigma^3}{6} \rho \), where \( \rho = N/L^3 \) is the number density, and of the temperature \( T \). The particles interact simultaneously via a short-range potential \( V_{SR} \) and a screened electrostatic repulsive interaction \( V_Y \). The short-range attraction is modeled for simplicity with the generalization to \( \alpha = 18 \) of the Lennard-Jones \( 2\alpha - \alpha \) potential, as proposed by Vliegenthart et al. \[30\]

\[
V_{SR}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{2\alpha} - \left( \frac{\sigma}{r} \right)^\alpha \right],
\]

where \( \epsilon \) is the depth of the potential. The parameters \( \sigma \) and \( \epsilon \) are chosen as units of length and energy respectively. We also consider \( k_B = 1 \). For this choice of \( \alpha \) the width of the attraction range is roughly \( 0.2\sigma \). The phase diagram of \( V_{SR}(r) \) has been studied previously \[30\] and it is characterized by a rather flat gas-liquid coexistence line, with a critical point located at \( T_c^{SR} \approx 0.43 \) and \( \phi_c^{SR} \approx 0.225 \).

The repulsive interaction is modeled by a Yukawa potential

\[
V_Y(r) = A \frac{e^{-r/\xi}}{r/\xi},
\]

characterized by an amplitude \( A \) and a screening length \( \xi \). We focus on the case \( \xi = 0.65\sigma \) and \( A = 8\epsilon \), for which the minimum of the pair potential \( V_{SR} + V_Y \) is located at \( r = 1.042\sigma \) corresponding to a potential energy \( E_{min} = -0.52\epsilon \). With the present choice of \( \alpha \) and \( \xi \), the ground state configuration of an isolated cluster is known to be the one-dimensional Bernal spiral, shown in Fig. II\[10\]. The Bernal spiral structure is composed of face-sharing tetrahedrons, resulting in three twisting strands of particles in such a way that each particle has six nearest neighbors. In this geometry, for large \( N \), the potential energy per particle \( E \) is \( E = -1.36 + 2.10/N \) (always in units of \( \epsilon \)). In the bulk of the spiral (far from side effects) \( E \) is about three times \( E_{min} \), confirming that the attractive interaction with the six neighbors provides most of the binding energy.

In parallel, we also study the case in which the magnitude of the attractive part changes to mimic the dependence of the depletion interaction on polymer concentration \( \phi_p \). As in Ref. \[10\], we choose \( \epsilon/k_B T = -14\phi_p \), i.e. the attraction strength is assumed to depend linearly on the fraction of free volume occupied by polymers \( \phi_p \). In this case, as in experiments, \( T \) is kept constant to \( k_B T = 1 \). To study a model as close as possible to the experimental work of Ref. \[10\], we select \( \xi = 0.65\sigma \), \( A = 10\epsilon \), and \( \alpha = 10 \). For this value of \( \alpha \), \( r_{min} = 1.07\sigma \), in agreement with the position of the maximum in the radial distribution function \( g(r) \), as extracted from data reported in Ref. \[10\].

The dependence of the potential shape with \( \phi_p \) is shown in Fig 2. Note that \( V(r) \) changes from monotonically repulsive to repulsive with a local minimum (with \( V(r_{min}) > 0 \)). Finally, for \( \phi_p > 0.50 \), \( V(r) \) develops an attractive global minimum followed by a repulsive tail.

In the rest of the present work, we will name \( T \)-route and \( \phi_p \) route the two parallel set of simulations. The short-range nature of \( V_{SR} \) favors a very effective way to define pairs of bonded particles. Indeed, the resulting potential \( V(r) = V_{SR} + V_Y \) has a well defined maximum located approximatively where the short range attrac-
tion becomes negligible. In the following we will consider bonded (or nearest neighbors) all pairs of particles whose relative distance \( d < r_{\text{max}} \). In the \( T \)-route case, we fix \( r_{\text{max}} = 1.28 \sigma \), while in the \( \phi_p \) case the bond distance between two particles can be conveniently defined as \( 1.4 \sigma \).

In all simulations, time is measured in units of \( \sqrt{m \sigma^2/\epsilon} \). For numerical reasons, the repulsive potential is cut at \( r_c = 8 \sigma \), such that \( V_Y(r_c) \approx 4.2 \times 10^{-3} A \). All simulated state points are shown in Fig. 3. Equilibration is achieved with Newtonian dynamics, followed by a Brownian dynamics simulation, based on the scheme of Ref. 32, to produce equilibrium structures. In the case of Newtonian dynamics, the equation of motion have been integrated with a time step of \( \Delta t = 0.02 \). In the case of Brownian dynamics, \( \Delta t = 0.05 \) with a bare diffusion coefficient \( D_o = 0.005 \). Equilibration runs required, at the slowest states, more than \( 10^9 \) integration time steps, corresponding to about three months of computer time on a 1.6 GHz Pentium processor.

II. EQUILIBRATION

Simulations are started from high \( T \) (or correspondingly \( \phi_p = 0 \)) equilibrium configurations and quenched to the selected final state. During equilibration, a Berendsen thermostat with a time constant of 10 is active, to dissipate the energy released in the clustering process. Following the quench, the time evolution of the potential energy \( E \) shows a significant drop. Equilibration becomes slower the lower the final \( T \) or the larger \( \phi_p \). It also slows down on lowering the colloid packing fraction \( \phi_c \). The evolution of \( E \) following a quench is shown in Fig. 4 for the case \( \phi_c = 0.16 \). Around \( T \lesssim 0.07 \), equilibration cannot be achieved within the simulation time and dynamic arrest takes place. In these conditions, extremely slow (logarithmic in time) drift of \( E \) is still present at long times. To provide evidence that equilibrium is reached during the Newtonian simulation we check that \( E \) is independent on the previous history and that clusters reversibly breaks and reform on changing \( T \) or \( \phi_c \). Similar results are obtained following the \( \phi_p \)-path.

The equilibration process is characterised by the progressive formation of bonds between particles and the corresponding growth of particle’s aggregates, named clusters.

A quantification of the evolution of the structure of the system during equilibration can be provided by the structure factor \( S(q) \), defined as

\[
S(q) = \langle \frac{1}{N} \sum_{i,j} e^{-i\vec{q} \cdot (\vec{r}_i-\vec{r}_j)} \rangle \tag{3}
\]

where \( \vec{r}_i \) indicates the coordinates of particle \( i \). The \( S(q) \) evolution, shown in Fig. 4, is reminiscent of the initial stages of spinodal decomposition, showing a low \( q \) peak which grows in amplitude and moves to smaller and smaller \( q \) vectors. While in spinodal decomposition, the coarsening process proceeds endlessly, in the present case the evolution of the small \( q \) peak stops when equilibrium is reached. The presence of the low \( q \)-peak in \( S(q) \), at a finite wavevector, highlights the presence of an additional characteristic length scale in the system, discussed in more details in the next section.

Fig. 4 shows the evolution of the shape of the largest cluster for the case \( \phi_c = 0.125 \) and \( T = 0.08 \), one of the cases in which the average cluster size grows monotonically in time. It is interesting to observe that at short times, the shape of the larger cluster is rather ramified, the potential energy is still large and locally the structure is still very different from the six-coordinated ground...
state structure. Cluster arms are essentially composed by particles arranged along lines. At longer times, the cluster arms get thicker and thicker, and the local configuration approaches the characteristic one of the Bernal spiral, even if some parts of the original branching points persist in the final structure favoring the formation of a gel network. The evolution of the shape, complemented by the time dependence of $E$, suggests that at large attraction strengths (low $T$ or large $\phi_p$), the equilibration process can be conceptually separated into two parts: an initial relaxation which is closely reminiscent of the one which would take place if the potential was purely attractive, followed by a second rearrangement which sets in only after the coordination number has become significant. At this point the competition of the long range repulsion enters into play, forcing thereby the system to rearrange into the expected local configuration. This competition results also in a non-monotonic evolution, during the equilibration, of the mean cluster size, at some state points.

III. EQUILIBRIUM PROPERTIES: STATICS

A. Potential Energy

The upper panel of Fig. 7 shows the $T$ dependence of $E/E_{\text{min}}$ at the studied values of $\phi_c$. Around $T \approx 0.2$, $E$ becomes negative, suggesting that the short-range attractive interaction becomes relevant. For lower $T$, $0.1 < T < 0.2$, $E$ drops significantly, quickly reaching below $T = 0.1$ a value compatible with the ground state Bernal spiral configuration (also shown), once the vibrational components are properly accounted for. A similar behaviour is observed for the $\phi_p$ dependence, shown in the lower panel of Fig. 7. In the studied $\phi_c$-range, the $\phi_c$ dependence of $E$ is rather weak, especially for large attraction strengths.

B. Cluster Size Distribution

In this section we examine the cluster size distribution, as it evolves with $\phi_c$ and $T$. Standard algorithms are used to partition particles into clusters of size $s$ and to evaluate the cluster size distribution $n_s$ and its moments.
The first moment of the cluster size distribution
\[
<s> = \frac{\sum s n_s s}{\sum s n_s} = N/N_s
\] (4)
is connected to the inverse of the number of clusters \(N_s\), while the second moment \(<s_2>\) provides a representative measure of the average cluster size
\[
<s_2> = \frac{\sum s^2 n_s s}{\sum s n_s}
\] (5)

We also examine the connectivity properties of the equilibrium configurations. Configurations are considered percolating when, accounting for periodic boundary conditions, an infinite cluster is present. The boundary between a percolating and a non-percolating state point has been defined by the probability of observing infinite clusters in 50% of the configurations. To provide an estimate of the percolation locus we report in Fig. 3 the state points which are percolating. We note that, at this level, percolation is a geometric measure and it does not provide any information on the lifetime of the percolating cluster. Indeed, at \(\phi_c = 0.125\), percolation is present both at high \(T\), where we observe geometric percolation of clusters with bonds of very short life-time, and at low \(T\) where the particles are connected by energetic bonds of very long life time, as discussed below. The competition between geometric and energetic percolation results in a intermediate temperature window where the system does not percolate, i.e. in a re-entrant percolation locus.

The cluster size distribution \(n(s)\) is shown in Fig. 5. At \(T = 0.2\) (where \(E ≈ 0\) and hence no significant bonding exists) upon increasing \(\phi\), the distribution progressively develops a power-law dependence with an exponent \(τ\), consistent with the random percolation value \(τ ≈ -2.2\).\(^{33, 34}\) Percolation is reached when \(0.125 < \phi < 0.16\). At slightly lower \(T\), i.e. \(T = 0.15\), the picture remains qualitatively similar, except for a hint of non-monotonic behavior, around \(s ≈ 10 − 20\). On further lowering \(T\), the number of clusters of size \(s ≲ 10\) drops significantly, to eventually disappear at \(T = 0.07\). These results are observed at all studied densities.

To frame the results presented above, we recall information previously obtained in the study of the ground state energy of isolated cluster of different size.\(^{10}\) For a cluster size \(s ≲ 10\), the addition of a monomer to an existing cluster lowers the energy per particle, since the gain associated to the formation of an additional attractive short-range bond is not yet compensated by the increased number of repulsive interactions. However, when clusters have grown sufficiently, for \(s ≥ 10 − 20\), the energy driving force for growing is reduced, since the energy per particle does not significantly depend any longer on the cluster size.\(^{14}\) Isolated clusters results carry on to the interacting clusters case since the relatively small screening length does not produce a significant cluster-cluster interaction. Indeed, the effective cluster-cluster potential will be characterized, to a first approximation, by the same \(ξ\), which is short as compared to the distance between clusters.

Around \(T ≈ 0.2\), \(E(T = 0.2) ≈ 0\) and hence energy can not be the driving force for clustering. Thus, it is not a surprise that close to percolation \(n(s) ∝ s^{-\tau}\) with \(τ\) consistent with the random percolation value\(^{33, 34}\). The disappearance of clusters of size \(s ≲ 10\), which starts to be visible for \(T ≤ 0.1\), signals the progressive role of energy in controlling clustering. At the lowest investigated \(T\), energy has taken over and all clusters are formed by energetically convenient configurations. In this respect, we can think of the low \(T\) system as a fluid composed of super-aggregates, providing an effective renormalization of the concept of “monomer” in the fluid. The small cluster-cluster interaction energy may favor a re-establishment of the random percolation geometries and characteristic exponents, as discussed in the following.

Fig. 8 shows the \(T\) and \(\phi_c\) dependence of the second moment of the distribution, the average cluster size \(<s_2>\), defined in Eq.5 for all non-percolating state points. Apart from \(\phi = 0.16\), where configurations are percolating already before the physics of the short-range bonding sets in, percolation at small packing fractions is not reached at all temperatures we are able to equilibrate. At \(\phi = 0.125\), a non-monotonic dependence of \(<s_2>\) is observed, which we interpret as a crossover from the “random” percolation observed at high \(T\) to the bond-driven percolation, which becomes dominant at low \(T\). The \(\phi_c\) dependence of \(<s_2>\) is shown in the bottom panel. At all \(T\), a monotonic growth is observed.
C. Cluster shape

A pictorial description of the shape of the larger cluster observed in a typical configuration at \( \phi_c = 0.08 \) and \( \phi_c = 0.125 \) for different \( T \) is shown in Figs. 10 and 11. In both cases, a progressive change of shape of the largest cluster is observed on cooling. A close look to the figures shows that on cooling particles become locally tetrahedrally coordinated and that the loose high \( T \) bonding progressively crosses to a one dimensional arrangement of tetrahedrons. At the lowest \( T \), the clusters are composed by large segments of Bernal spiral structures joined in branching points, the latter providing the mechanism for network formation.

To quantify the cluster shape we study the the cluster size dependence of the cluster radius of gyration \( R_g \), defined as

\[
R_g = \left[ \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{R}_{CM})^2 \right]^{1/2}
\]

(6)

where \( \mathbf{R}_{CM} \) are the center of mass coordinates. For fractional aggregates, \( R_g \sim s^{1/d_f} \), where \( d_f \) indicates the fractal dimension. The observed behavior of the clusters shape is very different at high and low \( T \). Fig. 12 shows \( R_g \) vs \( s \) for two representative state points at \( T = 0.15 \), close to percolation. The typical shape of the cluster at these two state points is reported in Fig. 10 and Fig. 11.

When the cluster size is greater than 20 monomers, the fractal dimension is consistent with the random percolation value in three dimensions (\( d_f = 2.52 \) [33, 34]). This value confirms that at high \( T \), as discussed previously, the energetic of the bonds is negligible as compared to entropic effects and the cluster size grows on increasing \( \phi_c \), mostly due to the increase in the average number of particles with a relative distance less than \( r_{max} \). At low \( T \), an interesting phenomenon occurs, shown in Fig. 13.

The very small clusters (\( s < 10 \)) are rather compact.
and $d_f \approx 3$ and indeed, in this size interval, the energy per particle in the cluster decreases on increasing cluster size \cite{35}. For clusters with intermediate size $10 < s < 100$, $d_f \approx 1.25$, supporting the preferential one-dimensional nature of the elementary aggregation process, driven by the repulsive part of the potential. This $d_f$ value is observed for all equilibrium cluster phases in which clusters of size $10 < s < 100$ are dominant, with a small trend toward smaller values for smaller $T$ and $\phi_c$. This small $d_f$ value provides further evidence that in this size interval growth is essentially uniaxial, and that clusters of size 100 or less are essentially composed by pieces of Bernal spirals joined by few branching points \cite{10} (see Fig. 11 and Fig. 12). For larger $s$ values, a crossover toward $d_f \approx 2.52$ is observed. This crossover suggests that for larger clusters the one-dimensional bundles have branched a significant number of times, generating clusters whose geometry is again controlled by random percolation features. Pieces of Bernal spirals act as building blocks connected at branching points in a random fashion.

\section{D. Structure Factor}

As discussed in Sec. 11 the clustering process and the residual repulsive interactions between different clusters produce an additional low $q$ peak in $S(q)$, located well below the location of the nearest neighbor peak ($q \sigma \approx 2\pi$). Fig. 12 and Fig. 13 show respectively the $T$ and $\phi_c$ dependence of $S(q)$, in equilibrium. Data refer to both percolating and non-percolating state points. We observe no dependence of the position (either with $T$ or $\phi_c$) of the nearest-neighbour peak, consistent with the presence of a deep minimum in the interaction potential, which defines quite sharply the interparticle distance. The amplitude of the nearest-neighbour peak grows on decreasing $T$ or increasing $\phi_c$. The location of the cluster-cluster peak shows a weak $\phi_c$ dependence, almost absent at $T = 0.2$ (and higher $T$), but which becomes more relevant at very low $T$. We note that, on isothermally increasing $\phi_c$, the location of the peak does not change even when percolation is crossed. On the other hand, the $T$-dependence is significant and the location of the peak moves to smaller $q$ on decreasing $T$, suggesting the establishment of longer correlation lengths. The $T$ and $\phi_c$ trends are quite similar to those recently observed in concentrated protein solutions at low ionic strength \cite{19}. In particular, in that paper, the independence of the cluster peak position on $\phi_c$ was interpreted as evidence of a linear dependence of the equilibrium cluster size with $\phi_c$. Indeed, if clusters are assumed to be rather monodisperse in size and if the inverse of the peak position is assumed to be a measure of the inter-cluster distance, the number cluster density has also to be independent on $\phi_c$. It is worth stressing that, in one of the first papers addressing the possibility of equilibrium cluster phases in colloidal systems \cite{12,35}, the same relation between equilibrium cluster size and $\phi_c$ was presented, although its validity was limited to the case of clusters of size significantly larger than the one observed experimentally in Ref. \cite{19}, hinting to a wider validity of the relation suggested in Ref. 19. Here we note that the independence of the $S(q)$ cluster peak position with $\phi_c$ holds from very small $\phi_c$ up to values well beyond percolation, where an interpretation in terms of finite clusters relative distance is clearly not valid. In the present study (of non spherical clusters), we can access both $S(q)$ and the cluster size distribution. We note that, as shown in Fig. 14, the cluster size distribution is not peaked around a typical value. Actually, the cluster size is significantly non-monodisperse, especially close to percolation. We also note that neither $<s_1>$ nor $<s_2>$ (see Fig. 15) scale linearly with $\phi_c$, despite the constant position of the low $q$ peak in $S(q)$.

It would be relevant to understand how the parameters $A$ and $\xi$ entering the potential (see Eqs. 12), control...
the position of the cluster peak and its $T$ and $\phi_c$ dependence. In the case of spherical clusters, it was possible to associate the peak position to the average distance between clusters, since no percolation was observed. This explanation is not fully satisfactory for the present model, since, as can be seen in Fig. 15 for the case of $T = 0.2$, the location of the peak is clearly the same both in the non-percolating state $\phi = 0.125$ and in the percolating state $\phi = 0.16$. A better understanding of the quantities controlling the peak position is requested. A first attempt in this direction has been recently presented [14].

FIG. 14: Wavevector $q$ dependence of $S(q)$ at three different $T$ ($T = 0.07, 0.1, 0.2$) for the $T$-route case. For each $T$, data at three different $\phi_c$ are reported ($\phi_c = 0.08, 0.125, 0.16$).

FIG. 15: Wavevector $q$ dependence of $S(q)$ at three different $\phi_c$ ($\phi_c = 0.08, 0.125, 0.16$) for the $T$-route case. For each $\phi_c$, data at several different $T$ are reported.

FIG. 16: Average number of neighbors $<n>$ as a function of $T$ for different $\phi_c$ values. Note that, for all $\phi_c$, all curves approach the $<n> = 6$ value characteristic of the geometry of the Bernal spiral.

E. Local Order

A simple and useful indicator of local order is provided by the average number of nearest neighbors $<n>$ and by the associated distribution of nearest neighbors $P(n)$, which counts the fraction of particles surrounded by $n$ neighbors within $r_{max}$. As shown in Fig. 16, $<n>$ grows upon progressively lowering $T$, approaching, in a non-monotonous way, a coordination number of six.

Fig. 17 shows the $T$ evolution of the distribution $P(n)$. Again, a clear preference for local geometries with about six neighbors is displayed at low $T$ a condition which is hardly observed in other materials in which particle-particle interaction is spherically symmetric. The value $<n> = 6$ is consistent with a local geometry of face-sharing tetrahedra.

Another useful indicator of local order, which enables us to effectively quantify the local structure, is provided by the so-called local orientation order parameters $\bar{q}_{lm}(i)$ defined as,

$$\bar{q}_{lm}(i) \equiv \frac{1}{N_{bi}} \sum_{j=1}^{N_{bi}} Y_{lm}(\hat{r}_{ij})$$

(7)

where $N_{bi}$ is the set of bonded neighbors of a particle $i$. The unit vector $\hat{r}_{ij}$ specifies the orientation of the bond between particles $i$ and $j$. In a given coordinate frame, the orientation of the unit vector $\hat{r}_{ij}$ uniquely determines the polar and azimuthal angles $\theta_{ij}$ and $\phi_{ij}$. The $Y_{lm}(\theta_{ij}, \phi_{ij}) \equiv Y_{lm}(\hat{r}_{ij})$ are the corresponding spherical harmonics. Rotationally invariant local properties can be constructed by appropriate combinations of the $\bar{q}_{lm}(i)$. In particular, local order in crystalline solids, liquids and
colloidal gels, has been quantified focusing on

g_l(i) \equiv \left[ \frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{q}_{lm}(i)|^2 \right]^{1/2} \quad (8)

and

\hat{w}_l(i) \equiv w_l(i)/\left[ \sum_{m=-l}^{l} |\bar{q}_{lm}(i)|^2 \right]^{3/2} \quad (9)

with

w_l(i) \equiv \sum_{m_1, m_2, m_3, \ m_1 + m_2 + m_3 = 0} \left( \begin{array}{ccc} m_l & m_{l_1} & m_{l_2} \\ m_m & m_m & m_m \end{array} \right) \bar{q}_{m_1}(i)\bar{q}_{m_2}(i)\bar{q}_{m_3}(i). \quad (10)

The distributions of the $g_l$ and $\hat{w}_l$ parameters provide a sensitive measure of the local environment and bond organization. For example, dimers are characterized by $g_1 = 1$, $\hat{w}_1 = 0.13$ and $\hat{w}_1 = -0.09$. A local tetrahedral order is characterized by large negative values of $\hat{w}_6$, up to the value $-0.17$ for the icosahedron. For the perfect Bernal spiral of Fig. 14, the orientational order parameters are determined as $g_4 = 0.224$, $g_6 = 0.654$, $\hat{w}_4 = 0.08$ and $\hat{w}_6 = -0.148$. Fig. 18 shows the $q_4$, $q_6$, $\hat{w}_4$ and $\hat{w}_6$ distributions and how they evolve with decreasing temperature for $\phi = 0.125$. We note that, upon cooling, the progressive presence of dimers and small clusters disappears and the distributions evolve toward a limiting form which appears to be specific of the Bernal spiral type of cluster. At low $T$, and in particular below $T = 0.1$, all distributions peak close to the characteristic values of the Bernal spiral. The local orientation order parameters have been evaluated in the confocal experimental work of Ref. 11. There, it was shown that the experimental data are consistent with the Bernal geometry. In the analysis of the experimental data, the position of the particles in the perfect spiral geometry was subjected to some random displacements, to account for thermal fluctuations, possible intrinsic errors in the localization of the particles and polydispersity in size (and/or charge) in the samples. After this procedure, the sharp peaks displayed in Figs. 18 and 19 disappear and smooth distributions are obtained, which well compare with the experimental data.

Fig. 19 shows that, at low $T$, the distributions appear to be insensitive to $\phi_c$, in agreement with observations in 11 and supporting once more that the local structure around the majority of the particles is similar to the ground state structure provided by the Bernal spiral.
reaches the value $\approx \ldots$ we observe a very similar behaviour, with a very simi-
larization length not very different from the one observed
in the case of dynamic arrest in glass forming systems,
where the long time limit of $\langle r^2(t) \rangle$ remains proportional to $t$, but with a smaller and smaller coefficient.

A global view of the $T$ and $\phi_c$ dependence of the slow dynamics is shown in Fig. 21, where the long time limit of $\langle r^2(t) \rangle / 6 t$, i.e. the self diffusion coefficient $D$, is reported. While at high $T$ the diffusion coefficient approaches the bare self-diffusion coefficient, on cooling, in the same $T$ interval in which a substantial bonding takes place, $D$ drops several order of magnitudes, signaling a significant slowing down of the dynamics and the approach to a dynamically arrest state. The same behaviour is evident for the $\phi_p$ route, where $D$ approaches a very small value for $\phi_p \geq 1.1$.

It is interesting to note that for $\phi_c = 0.125$ and $\phi_c = 0.16$, the $T$ dependence of $D$ is compatible with a power law, with exponent $\gamma_D \approx 2.2$, not very different from the typical values of $\gamma_D$ predicted by MCT for simple liquids. The case of $\phi_c = 0.16$ is particularly interesting, since at all $T$, the instantaneous configuration of the system is percolating, providing a clear example of the difference between percolation and dynamic arrest. Vanishing of $D$ is observed only at very low $T$, well below percolation. It is tempting to state that, when the cluster-cluster interaction is weak as in the present case, dynamic arrest always requires the establishment of a percolating network of attractive bonds, though this is not a sufficient condition since the bond lifetime should be significantly long. When repulsive cluster-cluster interactions are not negligible, arrest at low $\phi_c$ can be generated in the absence of percolation via a Yukawa glass mechanism.

Another important quantity to characterize dynamic arrest (particularly relevant for attraction-driven slowing down\cite{32}), is the bond correlation function $\phi_B(t)$, defined as

$$\phi_B(t) = \langle \sum_{i<j} n_{ij}(t)n_{ij}(0) \rangle / \langle N_B(0) \rangle. \quad (11)$$

Here $n_{ij}(t)$ is 1 if two particles are bonded and 0 otherwise, while $N_B(0) \equiv \langle \sum_{i<j} n_{ij}(0) \rangle$ is the number of
bonds at $t = 0$. The average is taken over several different starting times. $\phi_B$ counts which fraction of bonds found at time $t = 0$ are still present after time $t$, independently from any breaking-reforming intermediate process.

Figure 22 shows the evolution of $\phi_B(t)$ with $T$ and $\phi_p$. When dynamics slows down, the shape of $\phi_B(t)$ is preserved at all $T$ or $\phi_p$. The shape can be modeled with high accuracy with a stretched exponential function $A exp(-(t/\tau)^\beta)$, with stretching exponent $\beta \approx 0.73$.

An estimate of the average bond lifetime $\tau_B$ can be defined as $\tau_B = \tau/\beta\Gamma(1/\beta)$, where $\tau$ and $\beta$ are calculated via stretched exponential fits and $\Gamma$ is the Euler Gamma function.

Fig.23 shows $\tau_B$ versus $T$. Analogous considerations to those reported above in discussing the $T$-dependence of $D$ apply. Indeed, $\tau_B(T)$ is consistent with a power law with exponent $\gamma_T$ varying between 3.5 and 4.0, larger than the one found for $D(T)$, but with consistent predictions for the diverging $T$.

We notice that at $T = 0.07$, dynamics is extremely slow and bonds are almost unbroken in the time window explored in the simulation. It would be interesting to find out if the $T$ dependence of $\tau_B$ crosses to a different functional form at low $T$ when all bonds are formed and if such cross-over bears some analogies to the cross-over from power-law to super Arrhenius observed in glass forming molecular systems. Unfortunately, as in the molecular glass cases, the time scale today available to simulation studies does not allow us to resolve this issue.

To further compare the arrest observed in the present system and the slowing down of the dynamics observed in other systems close to dynamic arrest, we calculate the collective intermediate scattering function $F(q,t)$, defined as,

$$F(\bar{q},t) = \langle \frac{1}{N} \sum_{i,j} e^{-i\bar{q}(\bar{r}_i(t)-\bar{r}_j(0))} \rangle$$

where the average is calculated over different starting initial times. Fig.24 shows the $q$-dependence of the $F(\bar{q},t)$
FIG. 24: Wavevector $q$ dependence of the intermediate scattering function $F(q,t)$ at $T = 0.07, 0.10, 0.12$ (from top to bottom) for $\phi_c = 0.16$. The reported $q\sigma$ values are respectively $0.33, 0.78, 1.56, 2.34, 3.12, 4.68$.

at three different $T$ values. The decay of the correlation functions does not show any appreciable intermediate plateau for any $q$. The functional form of the decay is strongly dependent on $q$, crossing from an almost $\log(t)$ decay at small $q$ to a less stretched decay at large $q$ values. At the lowest $T$ ($T = 0.07$), $F(q,t)$ does not decay to zero any longer, confirming that a non-ergodic state has been reached. The non-ergodic behaviour manifests for very small values of $q\sigma$, in the range of the low $q$ peak in $S(q)$, while ergodicity is restored at nearest neighbor length. Fig. 25 contrasts, at fixed $q$ value, the $T$-dependence of the dynamics. The shape of $F(q,t)$ is sufficiently different to conclude that time-temperature superposition does not hold for this observable. We also note that at very low $\phi_c$ ($\phi_c = 0.04$ or 0.08) all density correlation functions decay to zero, within the explored time window, suggesting that cluster diffusion allows for the decay of density fluctuation, even in the presence of a non-ergodic bond restructuring process. This suggests that, at low $\phi_c$, density fluctuations are ergodic in the absence of percolation.

V. CONCLUSIONS:

In this work we have presented a detailed analysis of the structural and dynamic properties of a colloidal dispersion in which the short range attraction is complemented by a screened electrostatic repulsion. We have studied one specific choice of the parameters controlling the repulsive potential. In particular, we have chosen a screening length comparable to the radius of the colloidal particles. For this screening length, a study of the ground state structure of isolated clusters showed that the preferential local structure is composed by a one-dimensional sequence of face-shared tetrahedra, generating a local six-coordinated structure and a Bernal spiral shape.

The collective behavior of the system is very much influenced by the competition between attraction and repulsion, which in the present model sets in when $T$ becomes smaller than 0.2 (in units of the depth of the attractive part). The relative location of the particles, which for $T \geq 0.2$ is mostly controlled by translational entropy, for $T \lesssim 0.2$ depends more and more on energetic factors. Between $T = 0.2$ and $T = 0.1$, the number of bonded pairs increases significantly, and the local structure evolves progressively toward the six-coordinated one characteristic of the Bernal spiral. At the lowest studied $T$, $T = 0.07$, the cluster shape becomes independent of $\phi_c$ and the ground state local configuration becomes dominant. The cluster size distributions at low $T$ show a very clear suppression of clusters of size $\lesssim 10$, the size requested for the establishment of a bulk component in the spiral configuration.

Although the majority of particles tends to preferentially sit in the 6-coordinated configuration, some particles are located in defective regions of the spiral, which act as branching points and favor the formation of large ramified fractal clusters, whose elementary units are spirals of finite size. It is interesting to investigate if the small energetic cost of branching allows us to model the spiral segments as re-normalized monomers. In support of this possibility, we have detected a progressive increase of the cluster fractal dimension for cluster of size $s \gtrsim 100$. We have also shown that, consistent with the ground state calculations, clusters of size $s \lesssim 10$ are almost spherical, while clusters of size $10 \lesssim s \lesssim 100$ are characterized by $d_f \approx 1.25$.

The one-dimensional growth followed by a dynamic arrest phenomenon, observed in this work is reminiscent of
the aggregation process in several protein solution systems [38, 39, 41, 42]. In this class of protein solutions, a variation in the external control parameters (temperature, ionic strength, pH) often trigger an aggregation process of proteins into cylindric clusters which, by branching mechanisms, form a macroscopic gel, similarly to what takes place in the system here investigated. Results reported in this work confirm that, as speculated in Ref. [15], there is a range of small but finite temperatures in which branching of the one dimensional structure is preferred to cluster breaking and that such branching does indeed help establishing a connected three dimensional network.

It is important to stress that the dynamic arrest mechanism observed in this work is very different from the one observed numerically for the case of $\xi \approx 1.2\sigma$ [15]. In that case, clusters grow mostly spherical and do not present branching points. The slowing down of the dynamics in the $\xi \approx 1.2\sigma$ case arises from the residual repulsive cluster cluster interaction, resulting in the formation of a cluster phase or a repulsive cluster glass, analogous to the mechanisms suggested for Wigner glass systems. Indeed, in the arrested state, no percolation was detected. The arrested state generated via a Wigner glass transition discussed in Ref. [15] and the one generated via branching of one-dimensional clusters discussed in this work, although differing only by modest changes in the experimental conditions, are probably characterized by significantly different visco-elastic properties. Indeed we expect that the Wigner glass will be much weaker than the stiff percolating structure generated by a continuous sequence of particles tightly bounded to six neighbors.

The system studied in this work is a good candidate for a thorough comparison with the slowing down characteristic of glass forming materials. The numeric "exact" equilibrium particle structure factor could be used as input in the mode coupling theory, along the lines theoretically suggested in Ref. [15] to provide a full comparison of the theoretical predictions for the arrest line as well as for the shape of the correlation functions. It would be interesting to quantify the role of the cluster pre-peak in the structure factor in the predicted slowing down of the dynamics.

Results presented in this work also provide further example of the existence of equilibrium cluster phases, a phenomenon which is recently receiving a considerable interest. Cluster phases have recently been investigated in systems as different as protein solutions [4, 6, 9], colloidal dispersions [1, 4, 6, 10], liposome [42], liposomal solutions [5, 11, 14, 15, 16, 17], star-polymers [11], aqueous solutions of silver iodide [13, 14], metal oxides [6] and in recent numerical studies [15, 16, 17, 20]. In all cases, the combination of the repulsive interactions with the short range attraction appears to be crucial in stabilizing the cluster phase. The high sensitivity of the cluster shape and the final topology of the arrested state on the detailed balance between range and amplitude of the attractive and repulsive part of the potential brought forward by this and previous studies add new challenges to the modern research in soft condensed matter and to the possible technological exploitations of these new materials.

A final remark concerns the use of an effective potential, with state-independent parameters for the description of systems in which the screening length can be a function of the colloid packing fraction and in which the significant changes in structure with $T$ (or concentration of depletant) may lead to relevant changes in the cluster surface potential or in the spatial distribution of ions. The similarity between the numerical data reported in this manuscript and the closely related experimental results suggest that, despite the approximation adopted in the numerical work, the essence of the arrest phenomenon is captured by the present models.

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[1] P. N. Segrè, V. Prasad, A. B. Schofield, and D. A. Weitz, Phys. Rev. Lett. 86, 6042 (2001).
[2] A. D. Dinsmore and D. A. Weitz, J. Phys.: Condens. Matter 14, 7581 (2002), 430.
[3] I. Mladenovic, W. Kegel, P. Bomans, and P. Frederik, J. Phys. Chem. B 107, 5717 (2003).
[4] A. Stradner, H. Sedgwick, F. Cardinaux, W. C. K. Poon, S. U. Egelaaf, and P. Schurenbergen, Nature pp. 492–495 (2004).
[5] H. Sedgwick, S. U. Egelaaf, and W. C. K. Poon, J. Phys.: Condens. Matter 16, 4913 (2004).
[6] P. Bagliani, E. Fratini, B. Lonetti, and S.-H. Chen, J. Phys.: Condens. Matter pp. S5003–S5022 (2004).
[7] I. L. Validzic, G. van Hooland, S. Oosterhout, and W. Kegel, Langmuir 20, 3435 (2004).
[8] F. Bordi, C. Cametti, M. Diociaiuti, and S. Sennato, Phys. Rev. E (2005), in press.
[9] H. Sedgwick, K. Kroy, A. Salonen, M. B. Robertson, S. U. Egelaaf, and W. C. K. Poon, Eur. Phys. J. E 16, 77 (2005).
[10] A. I. Campbell, V. J. Anderson, J. van Duijneveldt, and P. Bartlett (2005), condmat/0410208, Phys. Rev. Lett. (in press).
[11] E. Stiakakis, G. Petekidis, D. Vlassopoulos, C. N. Likos, H. Iatrou, N. Hadjichristidis, and J. Roovers (2004), preprint.
[12] J. Groenewold and W. K. Kegel, J. Phys. Chem. 105, 11702 (2003).
[13] J. Wu, Y. Liu, W.-R. Chen, J. Cao, and S. Chen, Phys. Rev. E 70, 050401 (2004).
[14] Y. Liu, W.-R. Chen, and S. Chen, J. Chem. Phys. 122, 044507 (2005).
[15] F. Sciortino, S. Mossa, E. Zaccarelli, and P. Tartaglia, Phys. Rev. Lett. 93, 1 (2004).
[16] N. Sator, A. Fierro, E. D. Gado, and A. Coniglio (2003), condmat/0312591.
[17] A. Coniglio, L. D. Arcangelis, E. D. Gado, A. Fierro, and N. Sator, J. Phys.: Condens. Matter pp. S4831–S4839 (2004).
[18] A. Imperio and L. Reatto, J. Phys.: Condens. Matter 16, 3769 (2004).
[19] S. Mossa, F. Sciortino, P. Tartaglia, and E. Zaccarelli, Langmuir pp. 10756–10763 (2004).
[20] A. Kumar and J. Wu, Coll. and Surf. A 299, 280 (1964).
[21] D. Wu, D. Chandler, and B. Smit, J. Phys. Chem. 96, 4077 (1992).
[22] M. W. Deem and D. Chandler, Phys. Rev. E 49, 4276 (1994).
[23] R. P. Sear, S. Chung, G. Markovich, W. M. Gelbart, and J. R. Heath, Phys. Rev. E 59, 6255 (1999).
[24] C. B. Muratov, Phys. Rev. E 66, 066108 (2002).
[25] S. K. Lai, W. J. Ma, W. van Megen, and I. K. Snook, Phys. Rev. E 56, 766 (1997).
[26] S. K. Lai and G. F. Wang, Phys. Rev. E 58, 3072 (1998).
[27] J. Bosse and S. D. Wilke, Phys. Rev. Lett. 80, 1260 (1998).
[28] G. F. Wang and S. K. Lai, Phys. Rev. Lett. 82, 3645 (1999).
[29] J. D. Bernal, Proc. Royal Soc. (London) A 299, 280 (1964).
[30] G. A. Vliegenthart, J. Lodge, and H. N. W. Lekkerkerker, Physica A p. 378 (1999).
[31] In Ref. [11], the parameter $A$ was estimated as $30k_BT$. However, this value is too high, and the potential is always positive at the considered $\phi_p$ values. Thus, we chose the value of 10.
[32] M. Allen and D. Tildesley, Computer simulation of Liquids (Oxford University Press, Oxford, England, 1989).
[33] S. Torquato, Random Heterogeneous Materials: Microstructure and Macroscopic Properties (Springer-Verlag, New York, 2002).
[34] D. Stauffer and A. Aharony, Introduction to Percolation Theory (Taylor and Francis, London, 1992), 2nd ed.
[35] J. Groenewold and W. Kegel, J. Phys.: Condens. Matter 16, S4877 (2004).
[36] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B 28, 784 (1983).
[37] E. Zaccarelli, F. Sciortino, and P. Tartaglia, J. Phys.: Condens. Matter 16, 4849 (2001).
[38] T. Nicolai, C. Urban, and P. Schurtenberger, J. Coll. Inter. Sci. 240, 419 (2001).
[39] M. Pouzot, T. Nicolai, D. Durand, and L. Benyahia, Macromol. 37, 614 (2004).
[40] D. Renard, M. A. V. Axels, J. Lefebvre, and F. Boue, Biopolymers 39, 149 (1995).
[41] M. Manno, P. L. San Biagio, and M. U. Palma, Proteins: Structure, Function and Bioinformatics 55, 169 (2004).
[42] B. Ruzicka, L. Zulian, and G. Ruocco, Physical Review Letters 93, 258301 (2004).
[43] F. Bordi, C. Cametti, T. Gili, D. Gaudino, and S. Sennato, Bioelectrochemistry pp. 99–106 (2003).
[44] F. Bordi, C. Cametti, M. Diociaiuti, D. Gaudino, T. Gili, and S. Sennato, Langmuir 20, 5214 (2004).
[45] S. Sennato, F. Bordi, and C. Cametti, J. Chem. Phys. 123, 4936–4940 (2003).
[46] S. Sennato, F. Bordi, and C. Cametti, Europhys. Lett. 68, 296 (2004).
[47] F. Bordi, C. Cametti, and S. Sennato, Chem. Phys. Lett. (in press) (2005).