

Structural origins of dynamical heterogeneity in colloidal gels

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We show by resolving single-particle dynamics as a function of contact number that dynamical heterogeneity in depletion colloidal gels must have more than one structural origin. Although the magnitude of dynamical heterogeneity of weak gels with cluster structure and strong gels with string structure is similar, the dependence of particle localization on contact number differs significantly in each. The observed transition between contact number dependent and independent dynamics for the weak and strong gels is abrupt. The results suggest that spatially heterogeneous dynamics cannot be a complete explanation of the dynamical heterogeneity of colloidal gels.

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Colloidal particle gels are systems with arrested dynamics due to attractive pair potential interactions. These slow dynamics are the basis of gel function in the chemical processing of ceramics and the stabilization of complex fluid formulations [1]. Colloidal gels display dynamical heterogeneity that is common to polymer, inorganic, and hard sphere glasses [2]. When prepared in the vicinity of phase boundaries, colloidal gels are a model for a broad class of materials that show competition between phase separation and dynamical arrest [3]. Thus, observations that test mechanistic descriptions of these properties are of broad interest to soft condensed matter physics [4]. In particular, identifying the structural origin of the complex, heterogeneous dynamics of colloidal gels can delineate the degree to which theoretical descriptions of dynamical arrest, such as mode coupling theory [5], universally describe the behavior of colloidal glasses and gels.

At high volume fraction ($\phi \sim 0.4$), short-range attractive interactions affect dynamical arrest by perturbing the same cage structure that leads to the hard sphere glass transition [6,7]. Dynamics are spatially heterogeneous due to the slow exchange of bound and free particles [8]. At lower $\phi \sim 0.2$, dynamical arrest is the result of the network formed by long-lived particle bonds due to the attractive pair potential. Here there is significant disagreement between direct simulation and mode coupling theory [9]. Spinodal decomposition may also trigger local densification and subsequent dynamical arrest [10–14].

In this paper we present confocal microscopy experiments that identify structural origins of dynamical heterogeneity in colloidal gels by resolving the dynamics of subpopulations of different contact number. We find that although gels with cluster and string structures show dynamical heterogeneity of similar magnitude, their dependence of the non-Gaussian dynamics on contact number differs significantly. This difference implies that spatially heterogeneous dynamics is not a universal explanation of the dynamical heterogeneity of colloidal gels. Dynamical heterogeneity is the nonexponential relaxation of time correlation functions, equivalent to non-Gaussian behavior of the van Hove self-correlation function

[2]. A potential origin of dynamical heterogeneity is spatially heterogeneous dynamics. It is an ensemble of locally exponential relaxations, each with a different decay time [15].

We earlier identified cluster and string structural regimes in colloidal depletion gels with colloid $\phi = 0.20$ [16]. The particles (diameter, $2a = 1.9 \mu\text{m}$) are poly(12-hydroxystearic acid) stabilized poly(methyl methacrylate) particles interacting through short-range attractions due to nonadsorbing polymer. The range of the potential is $R_g/a = 0.043$, where R_g is the radius of gyration of the nonadsorbing polystyrene [16]. The abrupt transition in dynamics, shown in Fig. 1, is controlled by the concentration of nonadsorbing polymer, c/c^* , where c^* is the overlap concentration. At the transition ($c/c^* \sim 0.42$), the attractive component of the pair potential, estimated from the Asakura-Oosawa (AO) potential, is $U_{\text{contact}}/k_B T = -19.4$. Because the particles are charged, the depth of this contact attraction is reduced by the effect of screened Coulombic repulsion.

We select two samples, one on each side of the transition shown in Fig. 1, and compare behavior. The first, at $c/c^* = 0.31$ ($U_{\text{AO,contact}}/k_B T = -14.2$), is in the cluster gel regime. The second, at $c/c^* = 0.77$ ($U_{\text{AO,contact}}/k_B T = -35.5$), is a gel with stringlike structure. Each gel is dynamically heterogeneous as shown by the non-Gaussian form of their van Hove self-correlation functions, $G_s(x, t)$ (Fig. 1, inset). As opposed to [8,17], we find that decomposition of $G_s(x, t)$ into two Gaussian populations of fast (free) particles and slow (bound) particles is not a general description of all the measured $G_s(x, t)$. Thus, to probe the origins of this dynamical heterogeneity, we resolve colloidal dynamics into subpopulations based on local contact number, quantified as the number of nearest neighbors within a distance specified by the first minimum of the radial distribution function. Because they are a sensitive indicator of dynamical heterogeneity in glasses [18,19], we investigate subpopulation effects in $\langle \Delta x^2(t) \rangle$ and $G_s(x, t)$.

To monitor the dynamics of contact number subpopulations, immediately prior to collecting a 2D time series ($75 \times 75 \mu\text{m}^2$; optical depth of field $\sim 550 \text{ nm}$; $\Delta t = 0.848 \text{ s}$), we rapidly scan a 3D volume of size sufficient ($75 \times 75 \times 30 \mu\text{m}^3$) to characterize the contact number distribution of particles in the layer. The typical separation between the start of a 3D volume scan and a 2D time series is 51 s. In each

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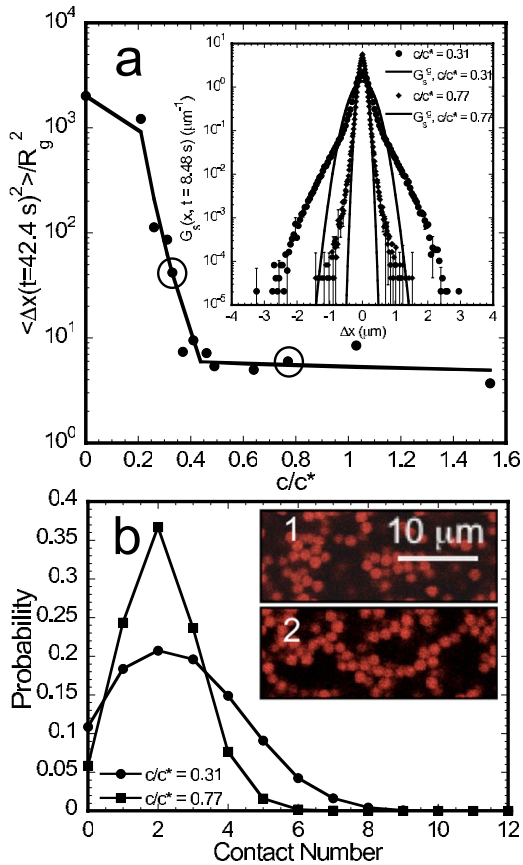


FIG. 1. (Color online) (a) Different dynamical regimes in colloidal depletion gels at $\phi=0.20$. The single-particle mean-squared displacement, $\langle \Delta x^2(t) \rangle$, scaled on the square of the range of the attraction, R_g^2 , is plotted at a characteristic time $t=42.4$ s. For $0.2 < c/c^* < 0.42$, where the gel forms a heterogeneous cluster structure, the characteristic single-particle displacement progressively decreases as the strength of attraction increases. For $c/c^* > 0.42$, the gels form a homogeneous stringlike structure in which the characteristic $\langle \Delta x^2(t) \rangle$ is relatively insensitive to attraction strength. The circled datum points, at $c/c^*=0.31$ and $c/c^*=0.77$, are the conditions selected for contact number subpopulation analysis in Figs. 2 and 3. As seen in the inset, both conditions show deviations of the van Hove self-correlation function, here plotted for $t=8.48$ s, from Gaussian behavior that are characteristic of dynamical heterogeneity. (b) The local contact number of the cluster and stringlike gels differ significantly. The stringlike gel has a narrow distribution peaked around two contacts. The cluster gel contains a significant fraction (33.5%) of particles with contact number of four and greater. Inset confocal microscopy images of gels at $c/c^*=0.31$ (1) and $c/c^*=0.77$ (2) are representative of clusters and strings, respectively. The scale bar represents 10 microns.

experiment, we track ~ 330 particles that fall within $\pm 1.3 \mu\text{m}$ of the 2D image plane to which a 3D contact number has been assigned based on the volume scan immediately previous. Data plotted in Figs. 2–4 are the subset of particles for which both 3D spatial and 2D dynamic information were collected.

Figure 2 shows $\langle \Delta x^2(t) \rangle$ for contact number resolved subpopulations of the two systems. As judged by the magnitude of the standard error of the mean from the six independent

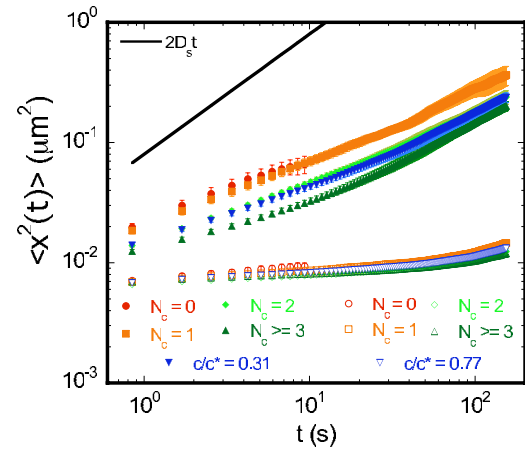


FIG. 2. (Color online) The mean-squared displacement, $\langle \Delta x^2(t) \rangle$, of contact number resolved subpopulations of the two gels ($c/c^*=0.31$ and $c/c^*=0.77$) are plotted versus time ($\phi=0.20$). The mean value of the displacement is also plotted for each condition. The line at upper left is the expected displacement for a hard particle at $\phi=0.20$. Contact number significantly affects the dynamics of particles in the cluster gel ($c/c^*=0.31$), but not in the string gel ($c/c^*=0.77$).

samples, data quality is good for all subpopulations for $t < 100$ s except for free particles ($N_c=0$) which are most likely to exit the 2D image during the experiment because of their higher mobility. Figure 2 is an experimental assessment of the effect of contact number on $\langle \Delta x^2(t) \rangle$ in colloidal gels. Qualitative differences in contact number effects for the two samples are apparent: For the weak, $c/c^*=0.31$ gel, mean displacement of particles with contact number zero and one is twice as large as that of particles with contact number three and greater. At $c/c^*=0.77$, the subpopulation $\langle \Delta x^2(t) \rangle$ is not a function of contact number. In both gels ($c/c^*=0.31$ and 0.77), exchange between the different contact number subpopulations is very small—we observe only a very limited number of bond breaking events over all samples at all times. Thus, the differences in Fig. 2 cannot be explained by this mechanism.

To understand the implications of the Fig. 2 differences for dynamical heterogeneity, in Fig. 3 we show $G_s(x, t)$ of each contact number subpopulation for the two gels. The particular delay time plotted is $\Delta t=8.48$ s. Comparing Figs. 3(a) and 3(b), the probability of large displacements ($\Delta x \sim a$) in $G_s(x, t)$ is a function of contact number for the cluster gel [Fig. 3(a), $c/c^*=0.31$] but not in the gel with stringlike structure [Fig. 3(b), $c/c^*=0.77$]. We test the data set by weighting each dynamic subpopulation by its (static) 3D contact number abundance and plot the sum for all weighted subpopulations as per the method of [20]. The good agreement shows that exchange between the different subpopulations is very small, consistent with our qualitative observations that no bond breaking events are observed over the duration of the time series.

For $c/c^*=0.31$, low contact number particles are significantly more mobile than high contact number particles, consistent with dynamical heterogeneity whose origin is spatially heterogeneous. However, Figs. 3(a) and 3(c) suggest

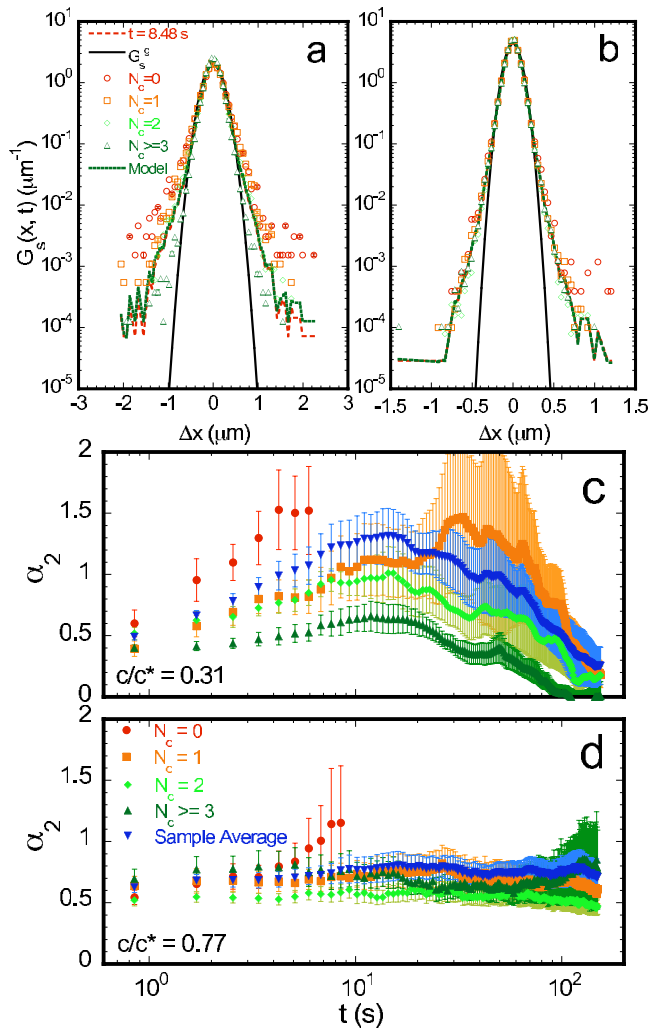


FIG. 3. (Color online) Subpopulation van Hove self-correlation function $G_s(x, t)$ for $c/c^* = 0.31$ (a) and $c/c^* = 0.77$ (b) at $t = 8.48$ s. At both conditions, the full-ensemble data set (dashed lines) is well described by the sum of the product of the relative abundance of each contact number subpopulation and its measure subpopulation $G_s(x, t)$ (model curve). The contact number dependence in $G_s(x, t)$ shown in (a) is reflected in contact number dependence of the non-Gaussian parameter, $\alpha_2(t)$, as plotted in (c). The maximum in $\alpha_2(t)$ in c is consistent with spatially heterogeneous dynamics in the cluster gel ($c/c^* = 0.31$). Contact number effects are not observed in either $G_s(x, t)$ or $\alpha_2(t)$ for the stringlike gel with $c/c^* = 0.77$. Because of their reduced abundance, subpopulations for $N_c > 3$ are plotted together.

that the decomposition of the spatially heterogeneous dynamics of cluster gels into two subpopulations of mobile and immobile particles, as per [8,17], is incomplete. Instead, heterogeneous dynamics in colloidal gels should be resolved by means of the full contact number distribution, since each subpopulation displays distinct dynamics. Furthermore, none of the contact number resolved $G_s(x, t)$ is itself Gaussian. Thus, some other component of dynamical heterogeneity is still needed to explain the non-Gaussian dynamics within each subpopulation.

Recent studies have found that the point of maximum dynamical heterogeneity in gels, as quantified by the four-

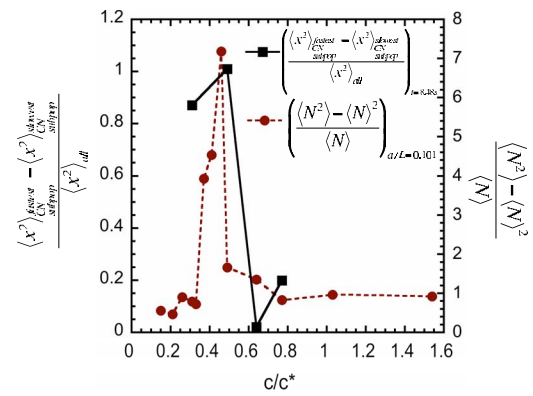


FIG. 4. (Color online) The transition from dynamical heterogeneity that is contact number dependent to behavior that is contact number independent is abrupt. At $t = 8.48$ s, the difference between the most and least mobile contact number subpopulations normalized by the system mean squared displacement is plotted for $c/c^* = 0.31, 0.49, 0.64$, and 0.77 . At $c/c^* \sim 0.5$, this measure of the spread in mobility of the contact number subpopulations decreases significantly. This transition coincides with a maximum in structural heterogeneity, here quantified by the number density fluctuation measure $(\langle N^2 \rangle - \langle N \rangle^2) / \langle N \rangle$, evaluated at the inverse length scale $a/L \sim 0.1$.

point dynamic susceptibility, χ_4 , scales with the system relaxation time [22–24]. Spatially heterogeneous dynamics is prominent at these long times [22]. Our confocal microscopy experiments address measurements at relatively short times, particularly for the strong gels that show significant localization. To address this short time behavior, in Fig. 3(c), we plot the subpopulation non-Gaussian parameter α_2 . The data show that the effect of contact number on the cluster gel α_2 persists over a range of times. For these weak gels, a point of maximum non-Gaussian behavior, $t^* \sim 14.4$ s, can be defined, consistent with supercooled liquids [18,21], the recent gel studies [22–24], and spatially heterogeneous dynamics. However, for the gel with stringlike structure ($c/c^* = 0.77$), the subpopulation $G_s(x, t)$ [Fig. 3(b)] and $\alpha_2(t)$ [Fig. 3(d)] are not a function of contact number. Interestingly, in the range $t \sim 5$ – 10 s, where the spread in contact number dynamics for the weak gels is greatest (cf. Fig. 2), the strong gel $\alpha_2 \sim 0.7$ is comparable to that of the weak gel α_2 . Thus, the two classes of gels exhibit similar magnitudes of dynamical heterogeneity, yet these dynamics are generated by quite different contact number dynamics. Although spatially heterogeneous dynamics could emerge at later times in the strong gels [22], the independence of dynamics on local structure suggests that spatially heterogeneous dynamics is not an explanation of the dynamical heterogeneity on the time scale observed.

We assessed the abruptness of the structural transition between the two types of contact number dynamics by testing two additional conditions, $c/c^* = 0.49$ and $c/c^* = 0.64$, each closer to the transition than the conditions discussed in Figs. 2 and 3. Contact number resolved dynamics at these additional conditions were measured, as per Fig. 2. The normalized difference between the fastest and slowest contact number resolved dynamics at the characteristic time $t = 8.48$ s is

plotted in Fig. 4 for all four conditions. This measure of the relative spread in the subpopulation dynamics changes abruptly at $c/c^* \sim 0.5$. The change in dynamical heterogeneity appears strongly coupled to a structural transition observed at $c^* \sim 0.42$ from [16], also plotted in Fig. 4.

We return to the earlier point that the magnitude of dynamical heterogeneity in colloidal systems is time dependent. For systems that display spatially heterogeneous dynamics, such as the weak gels studied here, dynamical heterogeneity displays a maximum that corresponds to a characteristic system relaxation time. Figure 3(d) indicates that measurements on the strong gel system were collected at times shorter than the characteristic system relaxation time, because a maximum in the non-Gaussian parameter is not observed within the duration accessible by our method. To further test the idea that dynamical heterogeneity can have two origins in colloidal gels, future experiments should study the effect of local contact number on string gel dynamical heterogeneity for durations much greater than reported in Fig. 3(d).

In conclusion, why does the contact number dependence of dynamical heterogeneity disappear in the strong, string gels? The deeper quench depth due to the increased depletion attraction might reduce rearrangements; however, almost no rearrangement events are observed in either the weak or the strong gels. Moreover, the abruptness of the Fig. 4 change argues against an effect that scales on $U_{AO,contact}/k_B T$, since this quantity varies continuously across the observed transition. We thus link the differences to the cluster and string

structures themselves. In particular, because of the absence of local variation in dynamics, the short-time dynamics of the strong gels appears better described as a homogeneously nonexponential process rather than a collection of exponential relaxations with spatially varying decay times [15]. This hypothesis is consistent with other instances in which coupling of dynamics on long-length scales gives rise to non-Gaussian dynamics that are spatially homogeneous. The first example, pointed out by Ref. [25], would be mode coupling theory itself, a case in which the slowing down of dynamics is due to collective interactions. In this case, structural heterogeneity, as evidenced by, for example, the number density fluctuations of Fig. 4, would be the underlying origin of the string gel dynamical heterogeneity, rather than the local connectivity. A second example of homogeneous nonexponential relaxation is the dynamics of networks of linear springs in a viscous solvent [26]. Here the single particle non-Gaussian dynamics arise due to the summation of normal modes with a distribution of relaxation times, rather than the summation of spatial regions with a distribution of relaxation times, as in spatially heterogeneous dynamics. These ideas would support a view of the stringlike gel as a network of fluctuating springs with extremely rare rearrangements, rather than as a suspension of diffusing clusters with long exchange times, as is appropriate for the weak cluster gel.

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