

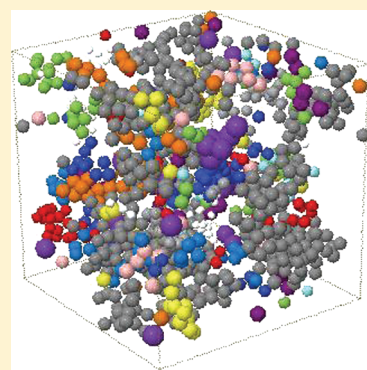
# Relaxation Process and Dynamical Heterogeneities in Chemical Gels: Critical Behavior of Self-Overlap and Its Fluctuation

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**ABSTRACT:** We study the dynamical behavior in chemical gelation, as the gelation threshold is approached from the sol phase. On the basis of the heterogeneous diffusion due to the cluster size distribution, as expected by the percolation theory, we predict the long time decay of the self-overlap as a power law in time  $t^{-3/2}$ . Moreover, under the hypothesis that the cluster diffusion coefficient decreases in size as a power law,  $s^{-x}$ , the fluctuation of the self-overlap,  $\chi_4(t)$ , exhibits growth at short time as  $t^{(3-\tau)/x}$ , where  $\tau$  is the cluster size distribution critical exponent. At longer times,  $\chi_4(t)$  decays as  $t^{-3/2}$  while, at intermediate times, it reaches a maximum at time  $t^*$ , which scales as  $s^{*x}$ , where  $s^*$  is the size of the critical cluster. Finally, the value of the maximum  $\chi_4(t^*)$  scales as the mean cluster size. The theoretical predictions are in agreement with molecular dynamic calculations in a model system, where spherical monomers are bonded by a finite extendable nonlinear elastic (FENE) potential.



## INTRODUCTION

In the context of the glass transition, the concept of dynamical heterogeneities has been very fecund.<sup>2–14</sup> The idea is that the relaxation process in glassy systems occurs through the correlated motion in space and time of groups of particles, whose size increases as the glass transition is approached. These heterogeneities have been studied quantitatively via the so-called dynamical susceptibility,<sup>4,15–17</sup>  $\chi_4(t) = N(\langle F^2(t) \rangle - \langle F(t) \rangle^2)$ , obtained as the fluctuation of a suitable time dependent correlator,  $F(t)$  (where  $N$  is the number of particles and  $\langle \dots \rangle$  is the ensemble average). Two correlators are usually considered: the self-intermediate scattering functions<sup>6,7</sup> and the time dependent overlap,<sup>15–17</sup> a quantity which was originally studied for spin glass models.<sup>4</sup> In usual glassy systems, the behavior of the dynamical susceptibility is essentially the same despite different choices of the correlator  $F(t)$ .<sup>5–17</sup> It grows as a function of time, reaches a maximum, and then decreases to zero consistently with the transient nature of the dynamical heterogeneities.

These concepts were later generalized to other complex systems, such as granular media<sup>18–21</sup> and attractive colloidal systems,<sup>22–26</sup> where behaviors qualitatively similar to those characterizing glassy systems are observed. On the other hand, in refs 27 and 28, completely different findings are found in models for chemical and colloidal gels at low volume fraction. In particular, in chemical gels,<sup>28</sup> it was shown that the dynamical susceptibility, defined as the fluctuation of the self-intermediate scattering function, in the infinite time limit, tends to a plateau. The value of such a plateau, in the limit of zero wave vector, coincides with the mean cluster size of bonded monomers, and consequently, it diverges as the volume fraction  $\phi$  reaches the gelation threshold  $\phi_c$  with percolation exponents. These predictions are confirmed by means of molecular dynamic simulations.

On the other hand, the fluctuation of the self-overlap was found numerically<sup>29</sup> to behave qualitatively similarly to the behavior found in glassy systems; namely, it reaches a maximum and then tends to zero in the long time limit.

To understand the different behaviors of the fluctuation of the self-overlap compared with the fluctuation of the self-intermediate scattering function, in this paper we study the self-overlap and its fluctuation, under the assumption that each cluster follows a simple relaxation process depending only on its size. The overall relaxation process is the sum of the relaxation process over all the clusters. Knowing the cluster size distribution, given by the percolation theory,<sup>30,31</sup>  $n(s) \propto s^{-\tau} e^{-s/s^*}$ , where  $s^*$  is the size of the critical cluster, and the size dependence of the cluster diffusion coefficient,  $D(s) \propto s^{-x}$ , where  $D(s)$  is the diffusion coefficient of the center of mass of a cluster of size  $s$ , we are able to obtain explicitly the behavior of the self-overlap and its fluctuation. In particular, we find that the self-overlap decays in the long time limit as a power law,  $t^{-3/2}$ . Its fluctuation,  $\chi_4(t)$ , exhibits a growth at short time as  $t^{(3-\tau)/x}$ . At long times,  $\chi_4(t)$  decays as  $t^{-3/2}$  while, at intermediate time, it reaches a maximum at time  $t^*$ , which scales as  $s^{*x}$ . Finally, the value of the maximum  $\chi_4(t^*) \propto (\phi_c - \phi)^{-\gamma}$  scales as the mean cluster size.

Using molecular dynamics simulations, we studied<sup>28,29,32</sup> a model for chemical gels, where spherical monomers are bonded by a finite extendable nonlinear elastic (FENE) potential,<sup>33,34</sup> and showed that the percolation transition is in the universality class of random percolation. In particular, the cluster size

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distribution scales with the exponent  $\tau = 2.1 \pm 0.2$ , the mean cluster size with  $\gamma = 1.8 \pm 0.1$ , and the connectedness length with  $\nu = 0.88 \pm 0.01$ , and the fractal dimension of large clusters is  $D_f = 2.4 \pm 0.1$ . Using these values and the value  $x \approx 0.75$  obtained for the size dependence of the cluster diffusion coefficient exponent, in the FENE model, we expect that at short time the dynamical susceptibility increases as a power law,  $\chi_4(t) \approx t^{1.2}$ , and reaches a maximum value,  $\chi_4(t^*)$ , at a time,  $t^*$ , both diverging at the threshold, respectively with exponents  $\gamma \sim 1.8$  and  $f = xD\nu \approx 1.6$ . The theoretical predictions are in good agreement with the numerical data.<sup>29</sup>

## DYNAMICAL ORDER PARAMETER: SELF-OVERLAP

Let us consider a system of randomly distributed monomers with fixed volume fraction,  $\phi$ . At time  $t = 0$ , permanent bonds are introduced at random between monomers at a distance  $r < R$ , where  $R$  is suitably chosen. In the section FENE Model for Permanent Gels, we will consider, in particular, the FENE model<sup>33,34</sup> for chemical gels; however, our arguments are independent of the details of the model.

In analogy with glassy systems,<sup>15–17</sup> the relaxation process can be described by a time-dependent order parameter  $q(t)$ , which measures the number of “overlapping” particles in two configurations separated by a time interval  $t$ , as follows:

$$q(t) = \frac{1}{N} \int d\vec{r}_1 d\vec{r}_2 \rho(\vec{r}_1, 0) \rho(\vec{r}_2, t) w(|\vec{r}_1 - \vec{r}_2|) \quad (1)$$

$$= \frac{1}{N} \sum_i \sum_j w(|\vec{r}_i(0) - \vec{r}_j(t)|)$$

where  $\rho(\vec{r}, t) = \sum_i \delta(\vec{r} - \vec{r}_i(t))$  is the density in  $\vec{r}$  at time  $t$  and where  $w(|\vec{r}_1 - \vec{r}_2|)$  is an “overlap” function, which can be taken equal to the Heaviside step function  $\Theta(|\vec{r}_1 - \vec{r}_2| - a)$ , that is, 1 for  $|\vec{r}_1 - \vec{r}_2| \leq a$  and zero otherwise (in glassy systems, the parameter  $a$  is usually chosen  $\sim 0.3$ ; the reasons for this choice are discussed in ref 7). In ref 5, the authors separate  $q(t)$  into self-components and distinct components,  $q(t) = q_{\text{self}}(t) + q_D(t)$ . The self-part,  $q_{\text{self}}(t)$ , which corresponds to the terms of eq 1 with  $i = j$  and measures the number of particles that move less than a distance  $a$  in a time interval  $t$  is given by the following:

$$q_{\text{self}}(t) = \frac{1}{N} \sum_i \Theta(\Delta \vec{r}_i(t) - a) \quad (2)$$

where  $\Delta \vec{r}_i(t) \equiv |\vec{r}_i(t) - \vec{r}_i(0)|$  is the displacement of the  $i$ -th particle in the time  $t$ . It was shown that the dominant term in eq 1 is on average given by the self-part.<sup>5</sup> In the following, we will also consider for simplicity the self-overlap, eq 2.

In the extreme case of very low volume fraction, where the system can be considered to be made of noninteracting monomers with the diffusion coefficient  $D$ , the self-part of the Van-Hove function<sup>35</sup> is a Gaussian, as follows:

$$G_{\text{self}}(\vec{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta(\vec{r} - \Delta \vec{r}_i(t)) \right\rangle = \frac{e^{-r^2/4Dt}}{(4\pi Dt)^{3/2}} \quad (3)$$

where  $\vec{r}$  is the distance traveled by a particle in a time  $t$ , and  $\langle \dots \rangle$  is the ensemble average. In this extremely dilute regime, the

self-overlap  $\langle q_{\text{self}}(t) \rangle$  is given by the following:

$$\langle q_{\text{self}}(t) \rangle = \int G_{\text{self}}(\vec{r}, t) \Theta(|\vec{r}| - a) d^3 \vec{r}$$

$$= \text{erf}(\alpha(t)) - \frac{2}{\sqrt{\pi}} \alpha(t) e^{-\alpha^2(t)} \quad (4)$$

where  $\alpha(t) \equiv a/(4Dt)^{1/2}$  and  $\text{erf}(z) = (2/\pi^{1/2}) \int_0^z \exp(-r^2) dr$  is the error function.

For higher volume fraction, the system is characterized by the cluster distribution  $n_s = N_s/N$ , where  $N_s$  is the number of clusters of size  $s$  and where the self-overlap can be written as the superposition of contributions as a result of different clusters. For a given bond configuration,  $\langle q_{\text{self}}(t) \rangle = 1/N \sum_{C_s} \sum_{i \in C_s} \langle \Theta(\Delta \vec{r}_i(t) - a) \rangle$ , where  $\sum_{C_s}$  is the sum over all the clusters  $C_s$  and where  $\sum_{i \in C_s}$  is the sum over the particle belonging to the cluster  $C_s$ . If the volume fraction is not too high, we can assume that particles belonging to clusters of size  $s$  diffuse with diffusion coefficient  $D(s)$ , depending only on  $s$ . Under this assumption, we obtain the following:

$$\langle q_{\text{self}}(t) \rangle = \sum_s n_s h(s, t) \quad (5)$$

where [...] is the average over bond configurations and

$$h(s, t) \equiv \text{erf}(\alpha(s, t)) - \frac{2}{\sqrt{\pi}} \alpha(s, t) e^{-\alpha^2(s, t)} \quad (6)$$

and

$$\alpha(s, t) \equiv a/\sqrt{4D(s)t} \quad (7)$$

Finally, using the following:

$$g(\alpha) \equiv \text{erf}(\alpha) - \frac{2}{\sqrt{\pi}} \alpha e^{-\alpha^2} \approx \begin{cases} 1 - \frac{2}{\sqrt{\pi}} \alpha e^{-\alpha^2}, & \alpha \geq 1 \\ \frac{4}{3\sqrt{\pi}} \alpha^3, & \alpha \ll 1. \end{cases} \quad (8)$$

from eqs 5 and 6, it follows the short and long time behaviors for the self-overlap:

$$\langle q_{\text{self}}(t) \rangle \approx \begin{cases} 1 - \frac{at^{-1/2}}{\sqrt{\pi}} \sum_s n_s D(s)^{-1/2} e^{-a^2/(4D(s)t)}, & \forall s \quad 4D(s)t \ll a^2 \\ \frac{a^3 t^{-3/2}}{6\sqrt{\pi}} \sum_s n_s D(s)^{-3/2}, & \forall s \quad 4D(s)t \gg a^2 \end{cases} \quad (9)$$

Equation 9 shows that as the clusters diffuse by a distance of the order of  $a$ , they contribute to the relaxation process by decreasing the self-overlap from its original value of 1, resulting in a power law decay of self-overlap,  $t^{-3/2}$ , for long times.

## DYNAMICAL SUSCEPTIBILITY: FLUCTUATION OF THE SELF-OVERLAP

In this section, we evaluate the dynamical susceptibility,  $\chi_4(t)$ , defined as the fluctuation of the self-overlap, for  $a$  greater than the connectedness length,  $\xi$ . In the extremely dilute regime, where particles do not interact,  $\chi_4(t) = 0$ . On increasing the volume fraction, particles form clusters, characterized by a cluster distribution  $n_s$ . At a low enough volume fraction, besides the assumption that particles belonging to clusters of size  $s$  diffuse

with diffusion coefficient  $D(s)$ , we make the additional hypothesis that clusters do not interact. Under such a hypothesis, we can neglect the contribution due to disconnected particles (we verified that this is in fact the case in the FENE model discussed in the section FENE Model for Permanent Gels), and  $\chi_4(t)$  can be written as a superposition of the contributions due to clusters as follows:

$$\chi_4(t) \approx \frac{1}{N} \left[ \sum_{C_s} \sum_{ij \in C_s} \langle \Theta(\Delta r_i(t) - a) \Theta(\Delta r_j(t) - a) \rangle - \langle \Theta(\Delta r_i(t) - a) \rangle \langle \Theta(\Delta r_j(t) - a) \rangle \right] \quad (10)$$

where [...] is the average over bond configurations and where the sums  $\sum_{C_s}$  and  $\sum_{ij \in C_s}$  are done over all clusters  $C_s$  and over each couple of particles belonging to the same cluster  $C_s$ , respectively. The displacement of the  $j$ -th particle in eq 10,  $\Delta r_j(t) \equiv |\vec{r}_j(t) - \vec{r}_j(0)|$ , can be written as  $\Delta r_j(t) = |\vec{r}_i(t) - \vec{r}_i(0) - \Delta_{ij}(t)|$ , where  $\Delta_{ij}(t) \equiv (\vec{r}_i(t) - \vec{r}_j(t)) - (\vec{r}_i(0) - \vec{r}_j(0))$ . Under the hypothesis that  $\Delta_{ij}(t) \ll \Delta r_i(t)$ ,  $\Delta r_j(t) \approx \Delta r_i(t)$  and being that  $\Theta(\Delta r_i(t) - a) = \Theta^2(\Delta r_i(t) - a)$ , eq 10 becomes the following:

$$\chi_4(t) \approx \frac{1}{N} \left[ \sum_{C_s} \sum_{ij \in C_s} \langle \Theta(\Delta r_i(t) - a) \rangle - \langle \Theta(\Delta r_i(t) - a) \rangle \langle \Theta(\Delta r_j(t) - a) \rangle \right] = \left[ \sum_s s^2 n_s h(s, t) (1 - h(s, t)) \right] \quad (11)$$

with  $h(s, t)$  given by eq 6. Because the dynamical susceptibility,  $\chi_4(t)$ , is different from zero for intermediate times, where the particle displacement is of the order of  $a$ , the hypothesis  $\Delta_{ij}(t) \ll \Delta r_i(t)$  is equivalent to  $\Delta_{ij}(t) \ll a$ . In chemical gels, if the variation in time of the distance between two particles belonging to the same cluster is at most equal to the connectedness length,  $\xi$ , then this condition applies for  $a \gg \xi$ .

It is easy to see that the function  $f(\alpha) = g(\alpha)(1 - g(\alpha))$ , with  $g(\alpha)$  given by eq 8, has a maximum for  $\alpha = \alpha_{\max} \approx 1.087652$  such that  $g(\alpha_{\max}) = 1/2$ . Consequently, the contribution to the dynamical susceptibility (eq 11) as a result of clusters of size  $s$ ,  $\chi_4(s, t)$ , has a maximum at  $t_{\max}(s)$  where  $h(s, t_{\max}(s)) = 1/2$ , namely  $t_{\max}(s) = a^2/(4D(s)\alpha_{\max}^2)$ , which is roughly the time for a cluster of size  $s$  to diffuse a distance of the order of  $a$ .

Using eq 8, we obtain the short and long time behaviors for the dynamical susceptibility as follows:

$$\chi_4(t) \approx \begin{cases} \sum_s s^2 n_s \frac{a(D(s)t)^{-1/2} e^{-a^2/(4D(s)t)}}{\sqrt{\pi}}, & \forall s \quad 4D(s)t \ll a^2 \\ t^{-3/2} \sum_s s^2 n_s \frac{a^3 D(s)^{-3/2}}{6\sqrt{\pi}}, & \forall s \quad 4D(s)t \gg a^2 \end{cases} \quad (12)$$

From percolation theory<sup>30,31</sup> in the sol phase, near the threshold, the cluster size distribution is given by  $n(s) \propto s^{-\tau} e^{-s/s^*}$  where  $s^*$  is the critical cluster of linear dimension  $\xi$ . Making the additional hypothesis that the cluster diffusion coefficient is given by  $D(s)D_1 s^{-x}$ , from eq 12 we easily obtain the following:

$$\chi_4(t) \propto \begin{cases} t^{(3-\tau)/x}, & 4D_{\max}t \ll a^2 \\ t^{-3/2}, & 4D_{\min}t \gg a^2 \end{cases} \quad (13)$$

where  $D_{\min}$  and  $D_{\max}$  are the diffusion coefficients of the maximal cluster and of the single monomer cluster, respectively. From

eqs 11, 6, and 8, it can be shown that  $\chi_4(t)$  has a maximum at a time  $t^*$  given by  $t^* = a^2/(4D(s^*)\alpha^{-2})$ , where  $\approx 1.16402$  is the solution of the equation

$$\int_0^\infty y^{2-\tau+x/2} e^{-yf'} (\bar{\alpha} y^{x/2}) dy = 0 \quad (14)$$

Inserting  $t^*$  in eq 11 and using<sup>30</sup> that  $-\gamma = (\tau - 3)^{D_p}$  and  $s^* \propto (\phi_c - \phi)^{-D_p}$ , we find that  $\chi_4(t^*)$  scales as the mean cluster size; in fact,

$$\chi_4(t^*) \approx s^{*(3-\tau)} \int_0^\infty y^{2-\tau} e^{-yf'} (\bar{\alpha} y^{x/2}) dy \quad (15)$$

## FENE MODEL FOR PERMANENT GELS

In this section, we check the theoretical predictions in a specific model for chemical gels. We consider a 3d system of  $N$  particles interacting with a soft potential given by the Weeks–Chandler–Andersen (WCA) potential as follows:<sup>36</sup>

$$U_{ij}^{\text{WCA}} = \begin{cases} 4\epsilon \left[ (\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 + \frac{1}{4} \right], & r_{ij} < 2^{1/6}\sigma \\ 0, & r_{ij} \geq 2^{1/6}\sigma \end{cases} \quad (16)$$

where  $r_{ij}$  is the distance between the particles  $i$  and  $j$ .

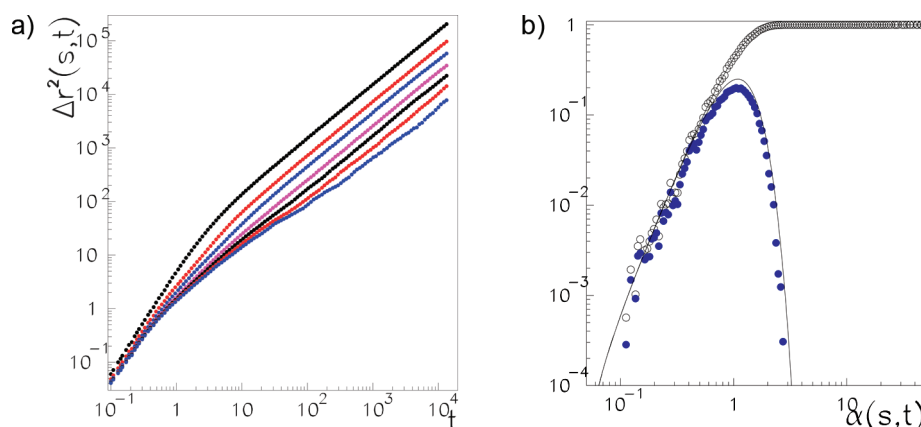
After the equilibration, at a given time  $t = 0$ , particles with distance less than  $R_0$  are permanently linked by adding an attractive potential as follows:

$$U_{ij}^{\text{FENE}} = \begin{cases} -0.5k_0 R_0^2 \ln[1 - (r_{ij}/R_0)^2], & r_{ij} < R_0 \\ \infty, & r_{ij} \geq R_0 \end{cases} \quad (17)$$

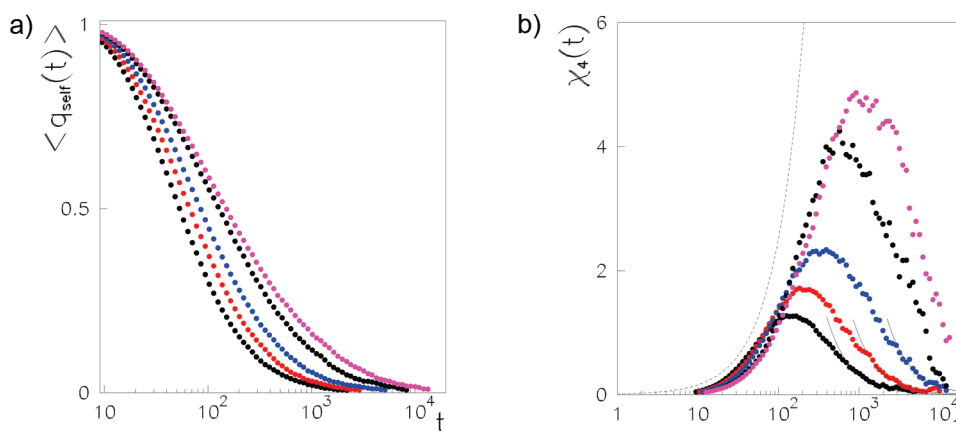
representing a finitely extendable nonlinear elastic (FENE) potential. It was introduced in ref 33 and is widely used to study linear polymers.<sup>34</sup> We choose  $k_0 = 30\epsilon/\sigma^2$  and  $R_0 = 1.5\sigma$  as in ref 34 to avoid any bond crossing.

The equations of motion are solved in the canonical ensemble (with a Nosé–Hoover thermostat) using the velocity–Verlet algorithm<sup>37</sup> with a time step  $\Delta t = 0.001\delta\tau$ , where  $\delta\tau = \sigma(m/\epsilon)^{1/2}$  is the standard unit time for a Lennard–Jones fluid and  $m$  is the mass of the particles. We use reduced units where the unit length is  $\sigma$ , the unit energy is  $\epsilon$ , and the Boltzmann constant  $k_B$  is set equal to 1. We choose periodic boundary conditions and average all the investigated quantities over 32 independent bond configurations. The temperature is fixed at  $T = 2$ , and values of the volume fraction  $\phi = \pi\sigma^3 N/6L^3$  (where  $L$  is the linear size of the simulation box in units of  $\sigma$ ) near the percolation threshold are chosen (from  $\phi = 0.08$  to  $\phi = 0.09$ ). We fix the linear size of the simulation box at  $L = 17.365$ .

Molecular dynamics simulations of this model were also performed in refs 28, 29, and 32. Using the percolation approach, the gel phase was identified as the state where a percolating cluster is present.<sup>38,39</sup> With a finite size scaling analysis,<sup>28,29,32</sup> it was obtained that the transition is in the universality class of random percolation. In particular, the cluster size distribution at the gelation threshold  $\phi_c = 0.09 \pm 0.01$  is given by  $n(s) \sim s^{-\tau}$ , with  $\tau = 2.1 \pm 0.2$ ; the mean cluster size in the sol phase near the threshold is  $S(\phi) = \sum s^2 n(s) \sim (\phi_c - \phi)^{-\gamma}$ , with  $\gamma = 1.8 \pm 0.1$ ; the connectedness length is  $\xi \sim (\phi_c - \phi)^{-\nu}$ , with  $\nu = 0.88 \pm 0.01$ ; and the fractal dimension of large clusters is  $D_f = 2.4 \pm 0.1$ .



**Figure 1.** (a) Mean squared displacement,  $[\langle \Delta r^2(s,t) \rangle]$ , of clusters for  $\phi = 0.0875$  and sizes  $s = 1, 3, 6, 10, 20, 40$ , and  $70$ . The diffusion coefficient, obtained from the fit  $\Delta r^2(s,t) \approx 6D(s)t$ , decreases as a power law  $D(s) \propto s^{-x}$ , with  $x \approx 0.75$ . (b) Self-overlap of clusters of size  $s$ , for  $\phi = 0.0875$ ,  $a = 15.0$ , and  $s = 9$  (black empty circles), and relative fluctuation (blue full circles) as a function of  $\alpha(s,t) = a(4D(s)t)^{-1/2}$ . The continuous curves are  $h(s,t) = \text{erf}(\alpha(s,t)) - 2\pi^{-1/2}\alpha(s,t) \exp(-\alpha^2(s,t))$  and  $h(s,t)(1 - h(s,t))$ , respectively. The only fitting parameter is  $D(s)$ , which is obtained from the mean squared displacement of clusters for  $s = 9$ .



**Figure 2.** (a) Self-overlap,  $\langle q_{\text{self}}(t) \rangle$ , for  $a = 15.0$  and  $\phi = 0.07, 0.075, 0.08, 0.085$ , and  $0.0875$  (from left to right). (b) Dynamical susceptibility,  $\chi_4(t)$ , for  $a = 15.0$  and  $\phi = 0.07, 0.075, 0.08, 0.085$ , and  $0.0875$  (from bottom to top). The dashed curve is a power law,  $t^{1.2}$ , and the continuous curves are  $t^{-3/2}$ .

In the sol phase, we study the dynamical behavior of the clusters. In particular, we measure the mean squared displacement of clusters of size  $s$ ,

$$\Delta r^2(s,t) = \left[ \frac{1}{sN_s} \sum_{C_s} \sum_{i \in C_s} \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle \right] \quad (18)$$

where  $\langle \dots \rangle$  is the thermal average over fixed bond configurations,  $[\dots]$  is the average over independent bond configurations, and  $N_s$  is the number of clusters of size  $s$ . After the short time ballistic regime,  $\Delta r^2(s,t)$  displays a diffusive behavior (in Figure 1a,  $[\langle \Delta r^2(s,t) \rangle]$  is plotted for  $\phi = 0.0875$  and different  $s$ ). We find that the diffusion coefficient of clusters,  $D(s)$ , obtained from the fit at long times,  $\Delta r^2(s,t) \approx 6D(s)t$ , decreases as a power law,  $D(s) \propto s^{-x}$ , with  $x \approx 0.75$ . As a result of a larger statistical ensemble, we consider this one a better estimate than the value given in ref 32 (i.e.,  $x \approx 0.67$ ).

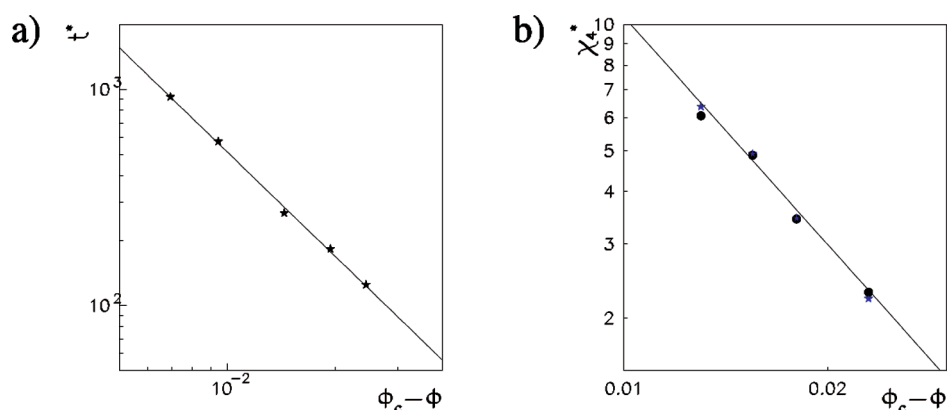
In Figure 1b, the self-overlap of clusters with the size  $s = 9$  and its fluctuation are plotted for  $\phi = 0.0875$  and  $a = 15$ . In agreement with the theoretical predictions obtained in the previous section, we find that the self-overlap of clusters of the size  $s$ ,  $q(s,t)$ , and its fluctuation,  $\chi_4(s,t)$ , are well fitted by  $h(s,t) = \text{erf}(\alpha(s,t)) - 2\pi^{-1/2}\alpha(s,t) \exp(-\alpha^2(s,t))$  and  $h(s,t)(1 - h(s,t))$ , respectively,

where  $h(s,t)$  is given by eq 6,  $\alpha(s,t) \equiv a/(4D(s)t)^{1/2}$ , and  $D(s)$  is the value obtained as fitting parameter from the mean squared displacement,  $\Delta r^2(s,t) \approx 6D(s)t$ , at given  $s$  and  $\phi$ . As expected from the theoretical predictions for large  $a$ , the agreement is good for all times and sizes.

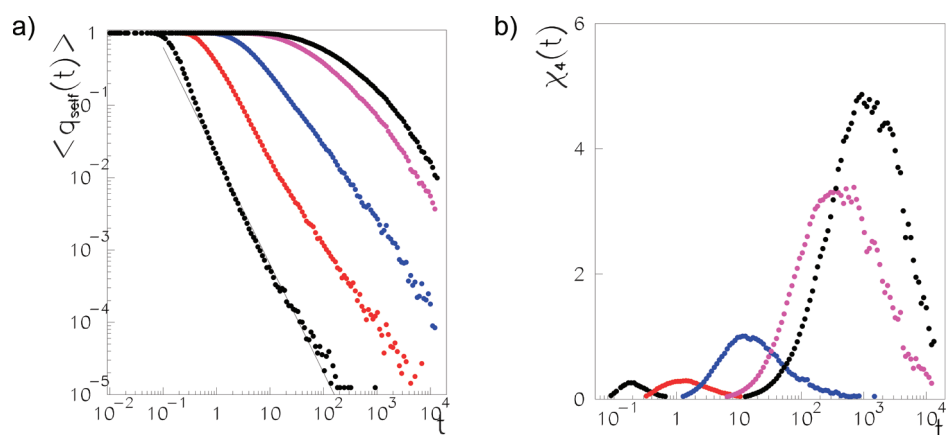
In Figure 2, the self-overlap,  $\langle q_{\text{self}}(t) \rangle$ , and the dynamical susceptibility,  $\chi_4(t)$ , are respectively plotted for  $a = 15.0$  and several volume fractions near the threshold. In agreement with theoretical predictions of previous sections,  $\chi_4(t)$  displays a peak, whose value increases as a function of the volume fraction. Moreover,  $\chi_4(t)$  increases at short times as  $t^{(3-\tau)/x}$ , with  $(3 - \tau)/x \sim 1.2$  (dashed curve in Figure 2b), and decreases at long times as  $t^{-3/2}$  (continuous curves in Figure 2b). A similar behavior is also found in the long time decay of the self-overlap. In Figure 3a, the time  $t^*$  where the dynamical susceptibility has the maximum is plotted as a function of  $\phi_c - \phi$  and is shown to diverge at the threshold with the exponent  $f \approx 1.6$ . In Figure 3b, the maximum value,  $\chi_4(t^*) \equiv \chi_4^*$ , is compared with the mean cluster size,  $S$ , and is shown to scale with the same exponent  $\gamma$ .

In Figure 4, the self-overlap,  $[\langle q_{\text{self}}(t) \rangle]$ , and its fluctuation,  $\chi_4(t)$ , are respectively plotted for  $\phi = 0.0875$  and several values of  $a$ . As we see in Figure 4a,  $[\langle q_{\text{self}}(t) \rangle]$  is well fitted by a power law,





**Figure 3.** (a) Time,  $t^*$ , where the dynamical susceptibility, for  $a = 15.0$ , has the maximum as a function of  $\phi_c - \phi$ , with  $\phi_c \approx 0.10$ . The continuous curve is a power law diverging with the exponent  $f = 1.6$ . (b) Maximum value of the dynamical susceptibility,  $\chi_4^*(\phi)$ , for  $a = 15.0$  (black circles), compared with the scaled mean cluster size  $S$  (blue stars), as a function of  $\phi_c - \phi$ , with  $\phi_c \approx 0.10$ . The continuous curve is a power law diverging with the exponent  $\gamma = 1.8$ .



**Figure 4.** (a) Self-overlap  $\langle q_{\text{self}}(t) \rangle$  for  $\phi = 0.0875$  and  $a = 0.3, 1.0, 3.0, 10.0$ , and  $15.0$  (from left to right). The continuous curve is a power law,  $at^{-3/2}$ , where  $a$  is the only fitting parameter. (b) Dynamical susceptibility,  $\chi_4(t)$ , for  $\phi = 0.0875$  and  $a = 0.3, 1.0, 3.0, 10.0$ , and  $15.0$  (from left to right).

$at^{-3/2}$ , for small  $a$  (see the particular case  $a = 0.3$ ), and long times. For small  $a$ , we have no explicit prediction for the behavior of  $\chi_4(t)$ . However, using the arguments of ref 28, we expect a strong dependence of the maximum on  $a$ , as shown in Figure 4b.

## CONCLUSIONS

Our analysis, under a simple hypothesis on cluster diffusion, predicts for a permanent gelling system a complex dynamical behavior, near the threshold, in agreement with the numerical data on a suitable model, where spherical monomers are bonded by a FENE potential.

In particular, in the diffusive regime, our calculations show that the dynamical susceptibility is a superposition of contributions as a result of different clusters, with each term having a maximum, at a time proportional to  $a^2/D(s)$ , which has a value proportional to  $s^2 n_s$ . We have checked these predictions in the FENE model, using molecular dynamics simulations at constant volume and temperature. We find that our data are in good agreement with the predictions, when the parameter  $a$  defining the window  $\Theta(r - a)$  of the self-overlap is large enough. Moreover, the peak of the fluctuation scales as the mean cluster size, therefore diverging at the percolation transition. In contrast to glassy systems, a strong length scale dependence on  $a$  is observed.

Moreover, again contrary to glassy systems, the fluctuation of the self-overlap considered here strongly differs from the fluctuation of the self-intermediate scattering function, which exhibits a plateau instead of a maximum. This different behavior is one of the major distinctive signs of gelation, compared with the (attractive or repulsive) glass transition.

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