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# Dynamical heterogeneities in irreversible gels: analogy with spin glasses

A Fierro<sup>1,2</sup>, T Abete<sup>2</sup>, A de Candia<sup>1,2,3</sup>, E Del Gado<sup>4</sup> and A Coniglio<sup>1,2,3</sup>

<sup>1</sup> INFN-CNR Coherentia, Dipartimento di Scienze Fisiche, Università degli Studi di Napoli 'Federico II', Complesso Universitario di Monte Sant'Angelo, Via Cintia, I-80126 Napoli, Italy

<sup>2</sup> Dipartimento di Scienze Fisiche, Università degli Studi di Napoli 'Federico II', Complesso Universitario di Monte Sant'Angelo, via Cintia, I-80126 Napoli, Italy

<sup>3</sup> INFN Udr di Napoli, Dipartimento di Scienze Fisiche, Università degli Studi di Napoli 'Federico II', Complesso Universitario di Monte Sant'Angelo, Via Cintia, I-80126 Napoli, Italy

<sup>4</sup> Department of Materials, Polymer Physics, ETH Zürich, CH-8093 Zürich, Switzerland

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## Abstract

We describe the sol–gel transition by introducing an order parameter, defined as the average of local variables, and its fluctuations. It can be shown that these quantities are related to percolation quantities, but in principle they can be measured without resorting to connectivity properties. In this framework it appears that the dynamical transition associated with gelation is a real thermodynamic transition, as happens in spin glasses. The strong analogies between the sol–gel transition and the spin glass transition are also discussed.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The sol–gel transition is a transition of a fluid (sol) into a disordered solid during which the diverging viscosity and the developing elastic modulus follow a power law behavior. Such a transition was interpreted [1, 2] in terms of the appearance of a percolating cluster of monomers linked by bonds [3]. This correspondence was confirmed by experimental measurements of the geometric properties of gels (for a review see [4] and references therein). More recently, random solidification for systems with permanent random constraints (such as, for example, vulcanized rubber and chemical gels) was studied at the mean-field level via the replica technique [5] and via field theoretical calculations [6]. In particular it was shown that the critical properties of the sol–gel transition and the percolation transition are identical.

We have investigated [7] the sol–gel transition both analytically and numerically with a model for permanent gels where bonds are modeled by a finitely extendible nonlinear elastic (FENE) potential [8, 9] between neighboring particles. In the first part of this paper (sections 2 and 3) we review the results recently obtained in this model, where the formation of permanent bonds between the particles leads to a percolation

transition, in the universality class of random percolation, and a dynamical transition typical of the sol–gel transition is observed. In the second part of the paper we describe the sol–gel transition by introducing an order parameter, defined as the average of local variables, and its fluctuations. It can be shown that these quantities are exactly related to percolation quantities, but in principle they can be measured without resorting to connectivity properties (see section 4). In this framework it appears that the dynamical transition associated with gelation is a real thermodynamic transition, as happens in spin glasses. The strong analogies between the sol–gel transition and the spin glass transition [5, 10] will be discussed in section 5.

Finally in section 6, we discuss the case of reversible gels, where bonds have a finite lifetime and the gelation transition, differently from permanent gels, does not correspond to a real thermodynamic transition [11].

## 2. Model and numerical simulations

We consider a 3d system of  $N$  particles interacting with a soft potential given by the Weeks–Chandler–Andersen (WCA)

potential [12]:

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

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

After the equilibration, particles distant less than  $R_0$  are linked by adding an attractive potential:

$$U_{ij}^{\text{FENE}} = \begin{cases} -0.5k_0R_0^2 \ln[1 - (r_{ij}/R_0)^2], & r_{ij} < R_0 \\ \infty, & r_{ij} \geq R_0 \end{cases} \quad (2)$$

representing the FENE potential, introduced in [8] and widely used to study linear polymers [9]. We choose  $k_0 = 30\epsilon/\sigma^2$  and  $R_0 = 1.5\sigma$  as in [9] in order to avoid any bond crossing and to use an integration time step  $\Delta t$  not too small. The introduction of the FENE potential leads to the formation of permanent bonds among all the particles whose distance at that time is smaller than  $R_0$ .

We have performed molecular dynamics simulations of this model: the equations of motion were solved in the canonical ensemble (with a Nosé–Hoover thermostat) using the velocity-Verlet algorithm [13] 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 particle. 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 the volume fraction  $\phi = \pi\sigma^3N/6L^3$  (where  $L$  is the linear size of the simulation box in units of  $\sigma$ ) is varied from below to above the percolation threshold. In agreement with the percolation approach, we identify the gel phase as the state in which there is a percolating cluster [1, 2]. Using a finite size scaling analysis [7] we find that the threshold is  $\phi_c = 0.09 \pm 0.01$  and the critical exponents coincide, within numerical error, with those of random percolation. In the following we fix the number of particles,  $N = 1000$ .

### 3. Self-intermediate scattering function and its fluctuations

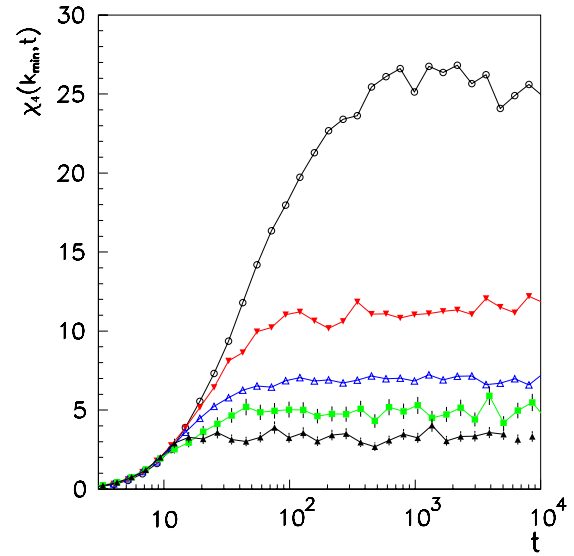
Relevant information on the relaxation dynamics over different length scales can be obtained from the self-intermediate scattering functions (ISF)  $F_s(k, t)$ :

$$F_s(k, t) = [\langle \Phi_s(k, t) \rangle], \quad (3)$$

where  $\langle \dots \rangle$  is the thermal average over a fixed bond configuration,  $[\dots]$  is the average over bond configurations of the system and

$$\Phi_s(k, t) = \frac{1}{N} \sum_{i=1}^N e^{ik \cdot (r_i(t) - r_i(0))}. \quad (4)$$

We find that, near the threshold,  $F_s(k, t)$  for a low wavevector is well fitted as a function of time by  $t^{-z} \exp(-(t/\tau)^\beta)$ ,



**Figure 1.** (Colour online) Dynamical susceptibility,  $\chi_4(k, t)$ , as a function of time for  $k = k_{\min}$  and different volume fractions  $\phi = 0.05, 0.06, 0.07, 0.08$  and  $0.09$  (from bottom to top).

with  $z$  and  $\beta$  not dependent on  $\phi$ . This form is obtained analytically from the cluster size distribution, and is confirmed by numerical data [14].

Here we review the discussion, presented in [7], about the behavior, near the sol–gel transition, of the fluctuations of the self-ISF:

$$\chi_4(k, t) = N[\langle |\Phi_s(k, t)|^2 \rangle - \langle \Phi_s(k, t) \rangle^2]. \quad (5)$$

Different from the behavior typically observed in glassy systems, we find that, for  $\phi < \phi_c$ ,  $\chi_4(k, t)$  is a monotonically increasing function of time tending to a plateau at a time of the order of the relaxation time  $\tau(k_{\min})$  (see figure 1, where  $\chi_4(k, t)$  is plotted for  $k = k_{\min}$  and different volume fractions). The value of the plateau diverges as the mean cluster size approaches the percolation threshold from the sol. For  $\phi \geq \phi_c$  the system is out of equilibrium and  $\chi_4(k, t)$  continues increasing as a function of time, without reaching any asymptotic value within the simulation time. In [7] it was shown that, for  $k \rightarrow 0$  and  $t \rightarrow \infty$ , the dynamical susceptibility  $\chi_4(k, t)$  tends to the mean cluster size. We define  $\chi_{\text{as}}(k, \phi) \equiv \lim_{N \rightarrow \infty} \lim_{t \rightarrow \infty} \chi_4(k, t)$ . Being  $\lim_{t \rightarrow \infty} \langle \Phi_s(k, t) \rangle = 0$ , we have

$$\chi_{\text{as}}(k, \phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \left[ \sum_{i,j=1}^N C_{ij}(k) \right], \quad (6)$$

where  $C_{ij}(k) = \lim_{t \rightarrow \infty} \langle e^{ik \cdot (r_i(t) - r_j(t))} e^{-ik \cdot (r_i(0) - r_j(0))} \rangle = |\langle e^{ik \cdot (r_i - r_j)} \rangle|^2$ . Here we have used the fact that, for large enough time  $t$ , the term  $e^{-ik \cdot (r_i(t) - r_j(t))}$  is statistically independent of  $e^{-ik \cdot (r_i(0) - r_j(0))}$ , so that we can factorize the thermal average. We separate the sum over connected pairs ( $\gamma_{ij} = 1$ , i.e. pairs belonging to the same cluster) and disconnected pairs ( $\gamma_{ij} = 0$ , i.e. pairs belonging to different

clusters), so that

$$\chi_{\text{as}}(k, \phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \left[ \sum_{i,j=1}^N |\langle e^{ik \cdot (r_i - r_j)} \rangle|^2 \right]$$

$$\lim_{N \rightarrow \infty} \frac{1}{N} \left[ \sum_{i,j=1}^N \gamma_{ij} C_{ij}(k) \right] + \frac{1}{N} \left[ \sum_{i,j=1}^N (1 - \gamma_{ij}) C_{ij}(k) \right]. \quad (7)$$

If particles  $i$  and  $j$  are not connected, for any fixed value of  $k > 0$ , the quantity  $C_{ij}(k)$  is  $O(1/N^2)$ .<sup>5</sup> As there are at most  $N^2$  disconnected pairs, the second term of the rhs of equation (7) is  $O(1/N)$  and can be neglected in the thermodynamical limit. For  $\phi < \phi_c$ , clusters will have at most a linear size of order  $\xi$ , so that the relative distance  $|r_i - r_j|$  of connected particles will be smaller than  $\xi$ . Therefore we have  $\lim_{k \rightarrow 0} \gamma_{ij} C_{ij}(k) = \gamma_{ij}$  and

$$\lim_{k \rightarrow 0} \chi_{\text{as}}(k, \phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \left[ \sum_{i,j=1}^N \gamma_{ij} \right] = S, \quad (9)$$

where  $S$  is the mean cluster size. As shown in [7], numerical data confirm this result.

In figure 2,  $\chi_4(k, \phi)$  is plotted for  $\phi = 0.09$  and different wavevectors. For each value of the wavevector,  $\chi_4(k, \phi)$  reaches a plateau after a characteristic time of the order of the relaxation time,  $\tau(k)$ . Using scaling arguments [7], we can write the asymptotic value as  $\chi_{\text{as}}(k, \phi) = k^{\eta-2} f(k\xi)$ , where  $f(z)$  is a function, which tends to a constant for small  $z$ , whereas it behaves as  $z^{\gamma/\nu}$  for large values of  $z$ , where  $2 - \eta = \gamma/\nu$ . As shown in [7], the data obtained in the FENE model support this scenario. In the inset of figure 2,  $\chi_{\text{as}}(k, \phi)$  is plotted at the threshold as a function of  $k$ : at low wavevectors the data are fitted with a power law,  $k^{\eta-2}$ , with an exponent  $2 - \eta = 2.03 \pm 0.02$ , consistent, within the numerical accuracy, with the prediction of random percolation [3]. All these results coherently show how in the present system the asymptotic value of the dynamical susceptibility is related to the cluster size. Our results not only indicate that the percolation exponents can be measured in a direct way, by developing techniques to measure the dynamical susceptibility, but they also state that the asymptotic value of the dynamical susceptibility plays the same role at the sol–gel transition as the static scattering function near the liquid–gas critical point.

#### 4. Order parameter and spatial correlation function

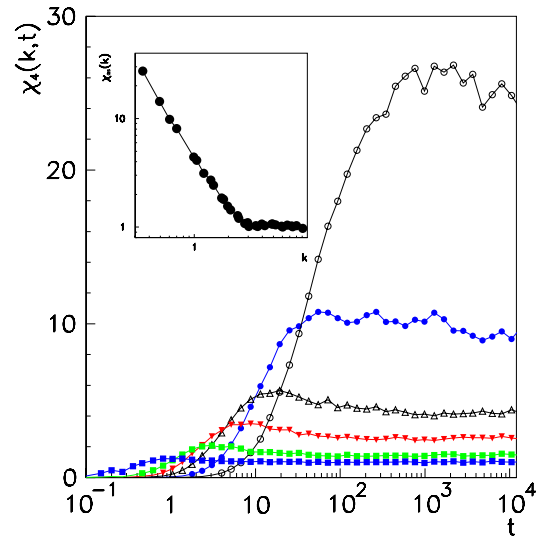
In the previous section we have discussed the dynamical behavior in a system approaching the gelation transition from the sol. Here we consider the static properties of the transition.

On the basis of results shown in section 3, in analogy with glasses and spin glasses [15], we suggest that the order

<sup>5</sup> We can write

$$\langle e^{-ik \cdot (r_i - r_j)} \rangle = \frac{1}{N} \int d^3 r e^{-ik \cdot r} \rho [h_{ij}(r) + 1], \quad (8)$$

where  $\rho = N/V$ ,  $h_{ij}(r) + 1 = g_{ij}(r)$  and  $(1/V)g_{ij}(r)$  gives the probability density of finding the particle  $i$  in  $r$ , given the particle  $j$  in the origin. For disconnected pairs, in the thermodynamic limit ( $N \rightarrow \infty$  and  $L \rightarrow \infty$  leaving the density  $\rho$  constant) the integral in equation (8) remains finite for any finite fixed  $k$ , so that the lhs of equation (8) is  $O(1/N)$ . The quantity  $C_{ij}(k)$ , being the square modulus of the lhs of equation (8), is therefore  $O(1/N^2)$ .



**Figure 2.** (Colour online) *Main frame:* dynamical susceptibility,  $\chi_4(k, t)$ , as a function of time for  $\phi = 0.09$  and  $k = 0.35, 0.61, 0.99, 1.40, 2.10, 3.96$  (from top to bottom). *Inset:* asymptotic values of the susceptibility,  $\chi_{\text{as}}(k, \phi_c)$  as a function of the wavevector  $k$ . Data are fitted with a power law  $\sim k^{-2.03 \pm 0.02}$ , in agreement with the exponent  $2 - \eta$  of random percolation.

parameter for the sol–gel transition is given by the  $k = 0$  limit of the long time limit of the self-ISF, namely

$$q_{\text{GEL}} \equiv \lim_{k \rightarrow 0} \lim_{t \rightarrow \infty} F_{\text{self}}(k, t) = \lim_{k \rightarrow 0} \frac{1}{N} \left[ \sum_{i=1}^N |\langle e^{ik \cdot r_i} \rangle|^2 \right], \quad (10)$$

where in this case  $\langle \dots \rangle$  is the time average<sup>6</sup> over a fixed bond configuration and  $[\dots]$  is the average over bond configurations of the system.

The meaning of the order parameter, equation (10), can be understood following the interesting arguments presented in [5], where a similar order parameter for the vulcanization transition is introduced. In the sol phase, all particles are *delocalized*, therefore, in the thermodynamic limit,  $\langle e^{ik \cdot r_j} \rangle = \delta_{k,0}$  for each  $j$ , and  $q_{\text{GEL}}$  is always zero. In the gel phase, some fraction of particles are *localized*. In the hypothesis that particle positions are distributed as Gaussians with average  $\langle r_j \rangle$  and mean squared displacement  $\xi_j^2$ ,  $\langle e^{ik \cdot r_j} \rangle$  can be written as  $e^{ik \cdot \langle r_j \rangle} e^{-\xi_j^2 k^2 / 2}$ . If particle  $j$  is *delocalized* ( $\xi_j \rightarrow \infty$ ), again  $|\langle e^{ik \cdot r_j} \rangle|^2 \rightarrow 0$  for each finite value of  $k$  (the  $k = 0$  value is instead 1). If particle  $j$  is *localized*,  $\xi_j$  is finite and the  $k \rightarrow 0$  limit is 1. Therefore  $q_{\text{GEL}}$  gives the density of *localized* particles. The main contribution to the localized particles comes from particles which are in the percolating cluster, but there is also a small fraction which comes from particles or clusters trapped inside the percolating cluster.

The order parameter, equation (10), can also be obtained, in analogy with spin glasses, considering two replicas of the system with the same bond configuration. We define

$$q = \frac{1}{N} \lim_{k \rightarrow 0} \sum_{i=1}^N e^{ik \cdot r_i^{(1)}} e^{-ik \cdot r_i^{(2)}}, \quad (11)$$

<sup>6</sup> The thermal average  $\langle e^{ik \cdot r_i} \rangle$  is zero both in the sol and in the gel phase.

where  $\mathbf{r}_i^{(1)}$  and  $\mathbf{r}_i^{(2)}$  are the positions of the particle  $i$  respectively in replicas 1 and 2. Introducing a coupling  $\epsilon \sum_i |\mathbf{r}_i^{(1)} - \mathbf{r}_i^{(2)}|^2$  between replicas, the order parameter, equation (10), can be written as

$$q_{\text{GEL}} = [\langle q \rangle_{1,2}], \quad (12)$$

where the average  $\langle \dots \rangle_{1,2}$  is the  $\epsilon \rightarrow 0$  limit of the thermal average over the two replicas. In this formalism, the fluctuations of the order parameter are given by

$$\chi_{\text{GEL}} = N [ \langle |q|^2 \rangle_{1,2} - |\langle q \rangle_{1,2}|^2 ]. \quad (13)$$

In particular, in the sol phase

$$\chi_{\text{GEL}} = \lim_{k,k' \rightarrow 0} \frac{1}{N} \left[ \sum_{i,j=1}^N \langle e^{ik \cdot (\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(1)})} \rangle \langle e^{-ik' \cdot (\mathbf{r}_i^{(2)} - \mathbf{r}_j^{(2)})} \rangle \right], \quad (14)$$

which coincides with  $\lim_{k \rightarrow 0} \chi_{\text{as}}(k, \phi)$ , equation (7), which we have shown to coincide with the mean cluster size.

Finally, in the sol phase, the pair correlation function can be defined in the  $k$ -space as

$$\tilde{p}(\mathbf{k}) = \frac{1}{N} \left[ \lim_{k' \rightarrow 0} \sum_{i,j=1}^N \langle e^{ik \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle \langle e^{-ik' \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle \right]. \quad (15)$$

Following the arguments already discussed (see footnote 5), we have

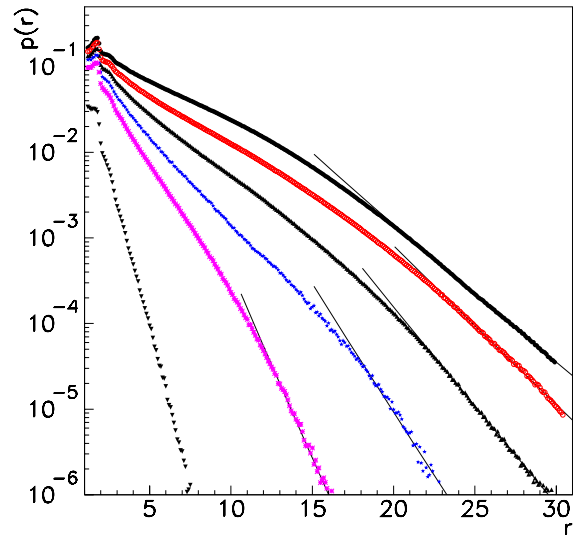
$$\tilde{p}(\mathbf{k}) = \frac{1}{N} \left[ \sum_{i,j=1}^N \gamma_{ij} \langle e^{ik \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle \right], \quad (16)$$

where again  $\gamma_{ij} = 1$  for  $i$  and  $j$  belonging to the same cluster and zero otherwise. The Fourier transform gives the pair connectedness function (see also [16]):

$$p(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} e^{ik \cdot \mathbf{r}} \tilde{p}(\mathbf{k}) = \frac{1}{N} \left[ \sum_{i,j=1}^N \gamma_{ij} \langle \delta(\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)) \rangle \right], \quad (17)$$

where  $p(\mathbf{r}) d\mathbf{r}$  gives the probability that a particle at the origin is connected to a particle in an element of volume  $d\mathbf{r}$  at a distance  $\mathbf{r}$ . From percolation theory [3] we know that  $p(r) \sim r^{-(d-2+\eta)} f_1(r/\xi)$ , where  $d$  is the spatial dimension and  $f_1(x)$  behaves as a constant for  $x \rightarrow 0$ , and goes to zero for  $x \rightarrow \infty$ . In figure 3,  $p(r)$  is plotted in the FENE model for different volume fractions in the sol phase. Near the gelation threshold, we find that  $p(r)$  is well fitted, at long distance, by  $r^{-(1+\eta)} e^{-r/\xi}$  (continuous curves in figure), where  $\xi$  increases as a function of the volume fraction. At low volume fractions the data are instead well fitted by simple exponentials.

In section 3, we have shown that  $\chi_{\text{as}}(k, \phi) = \frac{1}{N} [\sum_{i,j=1}^N |\langle e^{ik \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle|^2]$ , equation (7), has the same scaling form as  $\tilde{p}(\mathbf{k})$ . The advantage in using  $\chi_{\text{as}}(k, \phi)$  is that, in principle, it may be easier to detect experimentally. The spatial correlation function,  $G(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} e^{ik \cdot \mathbf{r}} \chi_{\text{as}}(k, \phi)$ , differs from  $p(\mathbf{r})$  only for a function whose integral over space is zero. In fact  $\int d\mathbf{r} G(\mathbf{r}) = \int d\mathbf{r} p(\mathbf{r}) = S$ .  $G(\mathbf{r})$ , measured in the FENE model, appears to be an oscillating function around  $p(\mathbf{r})$ .



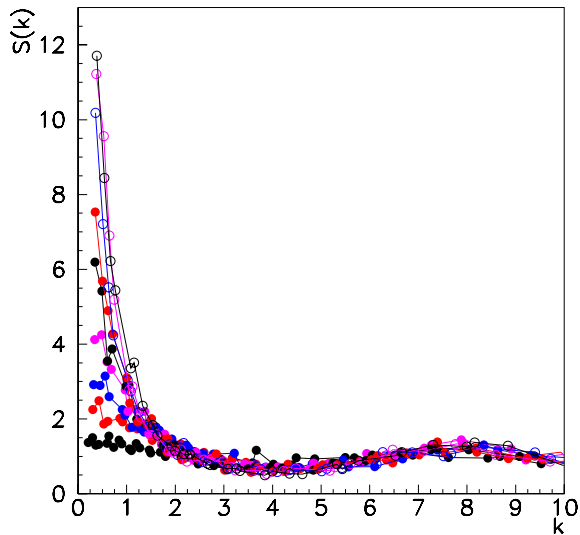
**Figure 3.** (Colour online) The pair connectedness function,  $p(r)$ , for  $\phi = 0.05, 0.08, 0.085, 0.09, 0.095, 0.1$  (from left to right). The curves in the figure are the fitting functions  $r^{-(1+\eta)} e^{-r/\xi}$ , with  $\xi$  increasing as a function of  $\phi$ .

## 5. Spin glass analogy

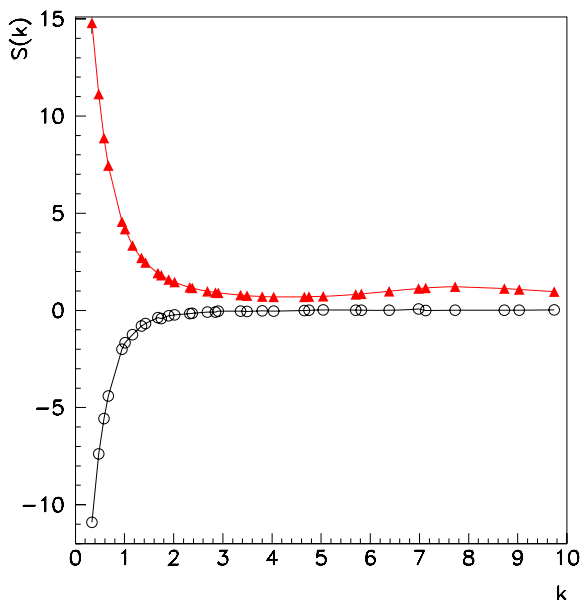
In this framework, the analogies between chemical gels and spin glasses appear evident. Note that in both equation (10) and in equation (7) the squared modulus of each term is considered. As in spin glasses, in fact, the corresponding quantities obtained without the squared modulus display trivial behaviors. Following the arguments of previous sections [5], it is easy to see that the density Fourier transform,  $\rho(\mathbf{k}) = \sum_{i=1}^N \langle e^{ik \cdot \mathbf{r}_i} \rangle$ , fails to distinguish between the sol and the gel, as the magnetization fails to distinguish between paramagnetic and spin glass states. Using the Gaussian approximation, we see that, even if some fraction of  $N$  particles are localized ( $\xi$  finite), their mean positions  $\langle \mathbf{r}_j \rangle$  are random, then for each finite value of  $\mathbf{k}$  the different terms add destructively in  $\rho(\mathbf{k}) = \sum_{i=1}^N \langle e^{ik \cdot \mathbf{r}_i} \rangle$  and the limit  $\mathbf{k} \rightarrow 0$  is always zero [5]. The squared modulus present in equation (10) allows us to avoid this destructive interference.

No sign of gelation is again seen in numerical and experimental measurements of the static structure factor,  $S(k) = \frac{1}{N} [\sum_{i,j} \langle e^{ik \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle]$ . In figure 4 the static structure factor,  $S(k)$ , is shown in the FENE model for chemical gels at different volume fractions, below and above the gelation threshold. As we see in the figure, the low  $k$  limit of the static structure factor,  $S(k)$ , is always small compared to both the number of particles and the mean cluster size. In figure 5, the contributions to the static structure factor of disconnected particles, and of connected ones, are respectively plotted. They apparently interfere in a destructive way. Again, the squared modulus present in equation (7) allows us to avoid this destructive interference.

Strong analogies between gels and spin glasses are also observed in the dynamical properties. In fact, the time-dependent order parameter is well fitted in both cases by  $t^{-z} \exp(-(t/\tau)^\beta)$  [14, 17] and in both cases the dynamical



**Figure 4.** (Colour online) Static structure factor,  $S(k)$ , for  $\phi = 0.02, 0.06, 0.07, 0.085, 0.09, 0.095, 0.1, 0.11, 0.12$  (full circles for  $\phi \leq \phi_c \sim 0.095$  and empty circles for  $\phi > \phi_c$ ). Continuous lines are a guide for the eyes.



**Figure 5.** (Colour online) Contribution to the static structure factor for  $\phi = 0.08$  of connected particles (full triangles) and disconnected ones (void circles). Continuous lines are a guide for the eyes.

susceptibility,  $\chi_4(t)$ , defined as the fluctuations of the time-dependent order parameter, increases as a function of time until a plateau value, which coincides with the static nonlinear susceptibility and diverges at the transition [10, 18]. As in spin glasses, in chemical gels the divergence of the static nonlinear susceptibility is also indicative of a true thermodynamic transition.

## 6. Reversible gels

In the previous sections we have shown that in chemical gels, where the structural arrest is related to the formation of

clusters of bonded particles, the dynamical susceptibility can be directly connected to the clusters. One can ask how this picture modifies in reversible gels, where bonds have a finite lifetime and the gelation transition does not correspond to a real thermodynamic transition.

This problem was studied [19] numerically using a DLVO type of interaction potential [20–22]. This model describes the presence of short range attraction well, due to depletion interactions, and long range repulsion, due to screening of Coulombic interactions, in a suspension of colloidal particles. The structural relaxation displays a slowing down with gel-like features at low temperatures and low volume fractions, due to the formation of persistent structures. By further increasing the volume fraction a crossover to a more glassy-like regime appears. In the gel-like regime the dynamical susceptibility exhibits a large plateau, dominated by clusters of long living bonds, as in chemical gels. Upon increasing the volume fraction, when the effect of the crowding of the particles starts to be present, the dynamical susceptibility instead displays a peak, as is usual in glassy systems. In the gel-like regime a suitable mean cluster size of clusters of monomers connected by ‘persistent’ bonds describes well the dynamical susceptibility [19]. However, due to the finite lifetime of the bonds the dynamical susceptibility tends to 1 and the gelation transition, differently from permanent gels, does not correspond to a real thermodynamic transition.

We suggest that these findings may be more generally related to reversible gelation [23–25]. In particular, in the copolymer micellar system L64 studied in [23] (where the short range attraction is due to effective intermicellar interaction), a transient gelation phenomenon followed by a structural arrest is also observed experimentally: for a fixed value of the temperature, as a function of the volume fraction, the viscosity increases, reaches a plateau and then increases again at higher volume fraction. In this process the rheological properties exhibit a crossover from gelation to a structural arrest typical of the glass transition. We suggest that the dynamical susceptibility, in the copolymer micellar system L64 studied in [23], displays the same type of behavior found in the DLVO model [19].

## Acknowledgments

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