Static and dynamic heterogeneities in a model for irreversible gelation

T. Abete, A. de Candia, E. Del Gado, A. Fierro, and A. Coniglio

Dipartimento di Scienze Fisiche, Università degli Studi di Napoli “Federico II”,
INFN, CNR-INFM Coherentia and CNISM, via Cintia, 80126 Napoli, Italy
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We study the structure and the dynamics in the formation of irreversible gels by means of molecular dynamics simulations of a model system where the gelation transition is due to the random percolation of permanent bonds between neighboring particles. We analyze the heterogeneities of the dynamics in terms of the fluctuations of the intermediate scattering functions: In the sol phase close to the percolation threshold, we find that this dynamical susceptibility increases with the time until it reaches a plateau. At the gelation threshold this plateau scales as a function of the wave vector \( k \) as \( k^{-\eta-2} \), with \( \eta \) being related to the decay of the percolation pair connectedness function. At the lowest wave vector, approaching the gelation threshold it diverges with the same exponent \( \gamma \) as the mean cluster size. These findings suggest an alternative way of measuring critical exponents in a system undergoing chemical gelation.

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In spite of the relevance of sol-gel processes in polymer physics, a comprehensive understanding of dynamics in irreversible gelation has not been achieved yet. Following the pioneering work by Flory and de Gennes [1], it is generally accepted that the divergence of the cluster size and the formation of a percolating network of permanent bonds is responsible for the sol-gel phase transition, with a critical increase of the viscosity coefficient and the onset of an elastic response close to the gelation transition. The question of how the cluster size can be related to a thermodynamic measurable quantity like the fluctuation of the order parameter near a critical point, is still, to our knowledge, an open question. A second question of what are the fundamental analogies and differences between the complex dynamics of polymer gels, colloidal gels, structural glasses and spin glasses has occasionally been discussed in the literature [2, 3], but never fully clarified.

In this paper we address these two questions by means of theoretical arguments and molecular dynamics (MD) simulations. We first study by MD the gel formation in a model system, where neighboring particles (monomers) are linked by permanent bonds to form clusters of different sizes. By varying the volume fraction \( \phi \) the system exhibits a percolation transition at \( \phi_c \), in the same universality class as random percolation. We analyze the dynamics in the sol phase, by means of the self intermediate scattering functions and show that the percolation transition coincides with a dynamical transition characterized first by stretched exponentials and at the percolation threshold by a power law behavior, as found in the experiments [4] and in some recent numerical works on the lattice [5]. To compare chemical gelation with the slow dynamics observed in colloidal gels or other disordered systems, such as glasses and spin-glasses, we measure the dynamic susceptibility defined as the fluctuations of the self intermediate scattering function. In supercooled liquids this or similar quantities have been introduced to characterize the behavior of dynamical heterogeneities [6, 7], which typically grow with time, reach a maximum, and then decrease at large time. This behavior, related to the growth of a dynamical correlation length, is a consequence of the transient nature of dynamic heterogeneities. In this model for chemical gelation, instead, we find that, approaching the gelation threshold in the sol phase, the dynamic susceptibility increases with time, until it reaches a plateau in the long time limit. This behavior is due to the presence of static heterogeneities (clusters), which being persistent do not lead to the decay of the non linear susceptibility. We argue in fact that the non linear dynamical susceptibility, in the infinite time limit, \( \chi_{\text{as}}(k, \phi) \) for \( k \to 0 \), coincides with the mean cluster size. The numerical data strongly support this result and show that, for small \( k \), it obeys the following scaling behavior \( \chi_{\text{as}}(k, \phi) = k^{-\gamma-2} f(k \xi) \), where \( \xi \sim (\phi_c - \phi)^{-\eta} \) is the connectedness length (the linear size of a critical cluster) and \( \nu \) the associated critical exponent, while \( 2 - \eta = \gamma / \nu \), \( \gamma \) being the mean cluster size exponent [8]. These relations link the mean cluster size to the fluctuations of the intermediate scattering function, which can be measured from light scattering experiments [9]. Therefore our results can be tested experimentally and offer a new alternative to previous methods [10], to measure percolation exponents in a sol-gel transition.

The model - We consider a 3d system of \( N = 1000 \) particles interacting via a Lennard-Jones potential, truncated in order to have only the repulsive part:

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

where \( r_{ij} \) is the distance between the particles \( i \) and \( j \). After a first equilibration, we introduce quenched bonds between particles whose relative distance is smaller than
representing a finitely extensible nonlinear elastic (FENE) [11]. The system is then further thermalized. We have chosen \( k_0 = 30 \epsilon / \sigma^2 \) and \( R_0 = 1.5 \sigma \) as in Ref. [11] and performed MD simulations in a box of linear size \( L \) (in units of \( \sigma \)) with periodic boundary conditions. The equations of motion were solved in the Verlet algorithm [12] with a time step \( \Delta t = 0.001 \delta t \), where \( \delta t = \sigma (m/\epsilon)^{1/2} \), with \( m \) the mass of particle. In our reduced units the unit length is \( \sigma \), the unit energy \( \epsilon \) and the Boltzmann constant \( k_B \) is set equal to 1. The temperature is fixed at \( T = 2 \) and the volume fraction \( \phi = \pi \sigma^2 N / 6 L^3 \) is varied from \( \phi = 0.02 \) to \( \phi = 0.2 \). By varying the volume fraction we find that the system undergoes a random percolation transition. From a standard finite size scaling analysis [8], we have obtained the percolation threshold \( \phi_c \), and the critical exponents \( \nu \) (which governs the power law divergence of the connectedness length \( \xi \sim |\phi - \phi_c|^{-\nu} \) as the critical point is approached from below) and \( \gamma \) (governing the power law divergence of the mean cluster size \( \chi \sim |\phi - \phi_c|^{-\gamma} \)). The results obtained are \( \phi_c = 0.10 \pm 0.02 \), with critical exponents \( \nu = 0.88 \pm 0.05 \) and \( \gamma = 1.8 \pm 0.1 \) in agreement with random percolation.

**Dynamical properties** - The dynamics at equilibrium is analyzed by measuring the self intermediate scattering function \( F_s(k,t) \) defined as \( F_s(k,t) = \langle |\Phi_s(k,t)|^2 \rangle \) where \( \Phi_s(k,t) = \frac{1}{N} \sum_{i,j=1}^N e^{i k \cdot (r_i(t) - r_j(0))} \). \( \langle \ldots \rangle \) is the thermal average for a fixed bond configuration and \([\ldots]\) is the average over the bond configurations. In our simulations the average is over 30 independent bond configurations. At low volume fractions \( F_s(k,t) \) decays to zero following an exponential behavior for all the wave vectors \( k \) considered. Increasing the volume fraction, close to the percolation threshold, at low wave vectors the long time decay starts to follow a stretched exponential behavior \( \sim e^{-(t/\tau)^\beta} \): The cluster size distribution has already started to widen and therefore, over sufficiently large length scales (small \( k \)), the behavior of \( F_s(k,t) \) is due to the contribution of different clusters, characterized by different relaxation times, whose superposition produces a detectable deviation from an exponential law. Close to \( \phi_c \) (see Fig. 1) the onset of a power law decay is observed at the lowest wave vector, \( k_{min} = 2 \pi / L \), indicating a critical slowing down due to the onset of a percolating cluster [13]. The behavior of \( F_s(k,t) \) for \( k = k_{min} \) (plotted in Fig. 2 as a function of the time for different volume fractions \( \phi \)) gives the relaxation dynamics over length scales of the order of the system size. As \( \phi \) increases towards \( \phi_c \), we observe a crossover from an exponential decay to a stretched exponential one, with \( \beta \) decreasing as a function of the volume fraction. At \( \phi_c \) the long time decay displays a power law behavior \( \sim t^{-c} \). If \( \phi \) increases further, the system is out of equilibrium. For long values of the waiting time, we find that \( c \) decreases until the long time decay becomes indistinguishable from a logarithm behavior and eventually a two step decay appears. These dynamical features well reproduce the experimental observations in different systems close to the gel transition [4] and agree with previous numerical results obtained on a lattice model [5].

![FIG. 1:](image)

We now analyze and discuss the behavior of the dynamical susceptibility \( \chi_4(k,t) \) associated to the fluctuations of \( \Phi_s(k,t) \), i.e. \( \chi_4(k,t) = N \left( \langle |\Phi_s(k,t)|^4 \rangle - \langle |\Phi_s(k,t)|^2 \rangle^2 \right) \). \( \chi_4(k_{min},t) \) is plotted in Fig. 3 for \( \phi \leq \phi_c \). Differently from the non monotonic behavior typically observed in supercooled glassy systems, we find that \( \chi_4(k_{min},t) \) increases with time until it reaches a plateau, whose value increases as a function of \( \phi \).

Indeed we argue that in the thermodynamic limit, when \( \phi \rightarrow 0 \) and \( t \rightarrow \infty \), \( \chi_4(k,t) \) tends to the mean cluster size. Being \( \lim_{t \rightarrow \infty} \langle \Phi_s(k,t) \rangle = 0 \), we have in the long time limit

\[
\lim_{t \rightarrow \infty} \chi_4(k,t) = \lim_{t \rightarrow \infty} \frac{1}{N} \sum_{i,j=1}^N \left( e^{i k \cdot (r_i(t) - r_j(0))} e^{-i k \cdot (r_i(0) - r_j(t))} \right)
\]

\[
= \frac{1}{N} \sum_{i,j=1}^N \left( e^{-i k \cdot (r_i(t) - r_j(t))} \right)^2
\]

(1)

In Eq. (1) we have considered that, for large enough time \( t \), the term \( e^{-i k \cdot (r_i(t) - r_j(t))} \) is statistically independent.
from $e^{-i\vec{k} \cdot (\vec{r}_i(0) - \vec{r}_j(0))}$, so that we can factorize the thermal average. In the last term of Eq. (1), we may now separate the sum over connected pairs ($\gamma_{ij} = 1$, that is pairs belonging to the same cluster), and disconnected ones ($\gamma_{ij} = 0$, that is pairs belonging to different clusters), so that

$$\lim_{t \to \infty} \chi_4(k, t) = \frac{1}{N} \sum_{i,j=1}^{N} \left[ \gamma_{ij} \left| \langle \exp(-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)) \rangle \right|^2 \right] + \frac{1}{N} \sum_{i,j=1}^{N} \left[ (1 - \gamma_{ij}) \left| \langle \exp(-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)) \rangle \right|^2 \right].$$

For $\phi < \phi_c$, clusters will have at most a linear size of order $\xi$, so that the relative distance $|\vec{r}_i - \vec{r}_j|$ of connected particles will be $\leq \xi$. Therefore, for $|\vec{k}| \ll \xi^{-1}$ and $\gamma_{ij} = 1$, we have $\langle \exp(-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)) \rangle = 1$. On the other hand, if particles $i$ and $j$ are not connected, $|\vec{r}_i - \vec{r}_j|$ can assume any value and the above argument does not apply. However, if particles $i$ and $j$ are not connected, we can write

$$\langle \exp(-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)) \rangle = \frac{1}{N} \int d^3\vec{r} e^{-i\vec{k} \cdot \vec{r}} \rho h_{ij}(\vec{r})$$

where $\rho = N/V$, $h_{ij}(\vec{r}) + 1 = g_{ij}(\vec{r})$ and $(1/V)g_{ij}(\vec{r})$ gives the probability density of finding the particle $i$ in $\vec{r}$, given the particle $j$ in the origin. We have used the fact that the Fourier transform of 1 is zero for any wave vector different from zero. The correlation function $h_{ij}(\vec{r})$ decays to zero at a finite distance, so that (3) is of order $O(1/N)$. As there are at most $N^2$ disconnected pairs, the second term in Eq. (2) is of order $O(1/N)$, so that it can be neglected in the thermodynamic limit. Finally, we have

$$\lim_{k \to 0} \lim_{t \to \infty} \chi_4(k, t) = \frac{1}{N} \sum_{i,j=1}^{N} \left[ \gamma_{ij} \right] \text{mean cluster size}.$$

In the inset of Fig. 3 the asymptotic value $\chi_{as}(k_{min}, \phi) = \lim_{t \to \infty} \chi_4(k_{min}, t)$ is plotted as a function of $(\phi_c - \phi)$ together with the mean cluster size. We find that, as the percolation threshold is approached from below, $\chi_{as}(k_{min}, \phi)$ shows a power law behavior with an exponent which, within the numerical accuracy, is in agreement with the value of the exponent $\gamma$ of the mean cluster size.

Using a standard scaling argument [8], we can easily predict the behavior of $\chi_{as}(k, \phi)$ for small $k$ close to $\phi_c$. Since $k$ scales as the inverse of a length, $\chi_{as}(k, \phi) = k^{\eta - 2} f(k\xi)$, where $\xi \sim (\phi_c - \phi)^{-\nu}$, $2 - \eta = \gamma/\nu$ and $f(z) \sim z^{\gamma/\nu}$ for small values $z$ and $f(z) \sim \text{const}$ for large values of $z$. Fig. 4 shows that the numerical data strongly support this scaling behavior.

In conclusion according to these results the percolation critical exponents in the sol-gel transition could be measured via the fluctuations of the self intermediate scattering functions by means of light scattering. Moreover our results confirm that one key difference between irreversible gelation due to chemical bonds and supercooled liquids close to the glass transition is that in irreversible
FIG. 4: **Main frame:** $\chi_{\alpha}(k, \phi_c)$ as a function of the wave vector $k$ and, from bottom to top, $\phi = 0.02, 0.05, 0.06, 0.07, 0.08, 0.085, 0.09, 0.095$. At $\phi_c$ the data are fitted with $\sim (k)^{\eta_{-2}}$ (full line), with $2 - \eta = 2.03 \pm 0.02$. **Inset:** Scaling plot of $\chi_{\alpha}(k, \phi)k^{2-\eta}$ as a function of $k^{-1/\nu}(\phi_c - \phi)$.

gelation the heterogeneities have a static nature (clusters). These clusters, on the other hand, affect the dynamics and as a consequence the dynamic transition coincides with the static transition, characterized by the divergence of a static correlation length (linear size of the clusters). In this respect the dynamical slowing down here is similar to the critical slowing down found close to a second order critical point, with the relaxation time diverging with a power law in the control parameters. Interestingly the behavior of the dynamical susceptibility is very similar to the one observed in spin glass models [14], where for long times it tends to the non linear static susceptibility, which diverges at the spin glass critical point. In fact, also in this case the dynamic transition is connected to the divergence of a static length.

What can we expect in colloidal gelation, where the bonds are not quenched and have a finite lifetime? In principle, due to finite bond lifetime, the clusters are not permanent anymore, consequently we expect a structural arrest with a dynamical susceptibility of the type found in glass forming liquid. This is in fact found in experimental investigations of colloidal suspension [15] and in some molecular dynamic simulations [16]. Interestingly enough, also in some spin glass models, by introducing interactions with finite lifetime, there is no divergence of the static susceptibility and one recovers the behavior of the dynamic susceptibility which is typical of supercooled liquids [14].

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