

Static and Dynamic Heterogeneities in a Model for Irreversible Gelation

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We study the structure and the dynamics in the formation of irreversible gels by means of molecular dynamics simulation 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 self-intermediate scattering functions: in the sol phase close to the percolation threshold, we find that this dynamic 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 η 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 γ 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 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 Letter 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 ϕ the system exhibits a percolation transition at ϕ_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 (ISF) and show that the percolation transition coincides with a dynamic 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-ISF. In supercooled liquids this or similar quantities have been introduced to characterize the behavior of dynamic 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 dynamic 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 dynamic susceptibility. We argue, in fact, that the dynamic susceptibility, in the infinite time limit, $\chi_{as}(k, \phi)$ for $k \rightarrow 0$, 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 $\chi_{as}(k, \phi) = k^{\eta-2} f(k\xi)$, where $\xi \sim (\phi_c - \phi)^{-\nu}$ is the connectedness length (the linear size of a critical cluster) and ν the associated critical exponent, while $2 - \eta = \gamma/\nu$, γ being the mean cluster size exponent [8]. These relations link the mean cluster size to the fluctuations of the ISF, which can be measured from light scattering experiments [9,10]. Therefore, our results can be tested experimentally and offer a new alternative to previous methods [11], to measure percolation exponents in a sol-gel transition.

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

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

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 R_0 by adding an attractive potential:

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

representing a finitely extendable nonlinear elastic

(FENE)[12]. The system is then further thermalized. We have chosen $k_0 = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$ as in Ref. [12] and performed MD simulations in a box of linear size L (in units of σ) with periodic boundary conditions. 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 $\delta\tau = \sigma(m/\epsilon)^{1/2}$, with m the mass of particle. In our reduced units the unit length is σ , the unit energy ϵ , and the Boltzmann constant k_B is set equal to 1. The temperature is fixed at $T = 2$ and the volume fraction $\phi = \pi\sigma^3 N/6L^3$ 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. For each value of ϕ we have carried out simulations of systems of sizes $L = 5, 8, 10, 20, 40$ and we have performed a standard finite size scaling analysis [8]. We have obtained [14] the percolation threshold ϕ_c , and the critical exponents ν (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 γ (governing the power law divergence of the mean cluster size $\chi \sim |\phi - \phi_c|^{-\gamma}$). The results obtained are $\phi_c = 0.100 \pm 0.002$, with critical exponents $\nu = 0.88 \pm 0.05$ and $\gamma = 1.8 \pm 0.1$, in agreement with random percolation.

Dynamic properties.—The dynamics has been investigated using a system made of $N = 1000$ particles for volume fractions ranging from $\phi = 0.02$ to $\phi = 0.2$. The dynamics at equilibrium is analyzed by measuring the self-ISF $F_s(k, t)$ defined as $F_s(k, t) = [\langle \Phi_s(k, t) \rangle]$, where $\Phi_s(k, t) = \frac{1}{N} \sum_{i=1}^N e^{ik \cdot [\bar{r}_i(t) - \bar{r}_i(0)]}$, $\langle \cdot \cdot \cdot \rangle$ is the thermal average for a fixed bond configuration, and $[\cdot \cdot \cdot]$ 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 ϕ_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 [15]. 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 ϕ) gives the relaxation dynamics over length scales of the order of the system size. As ϕ increases towards ϕ_c , we observe a crossover from an exponential decay to a stretched exponential one, with β decreasing as a function of the volume fraction. Note that the power law, t^{-c} , occurs at a value $\phi = 0.09$, which is the effective critical threshold for such a finite system. If ϕ

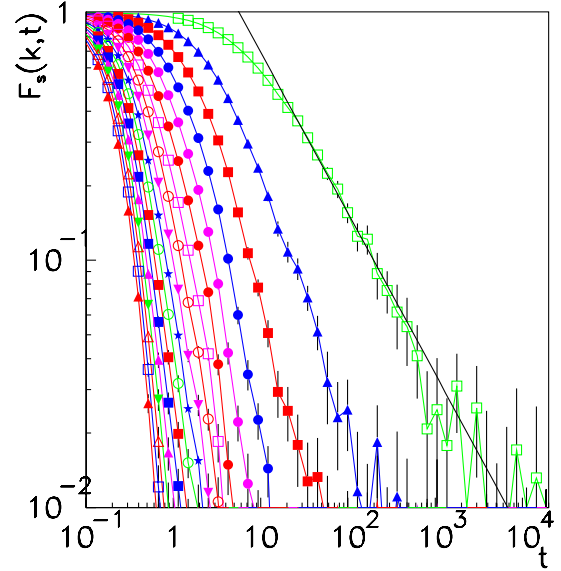


FIG. 1 (color online). $F_s(k, t)$ for decreasing values of k from left to right at $\phi = 0.09$ as a function of the time t . At $k = k_{\min} \simeq 0.35$ the data are fitted by a power law $\sim t^{-c}$ with $c = 0.65 \pm 0.03$ (straight line).

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 dynamic 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].

We now analyze and discuss the behavior of the dynamic susceptibility associated to the fluctuations of $\Phi_s(k, t)$, i.e.,

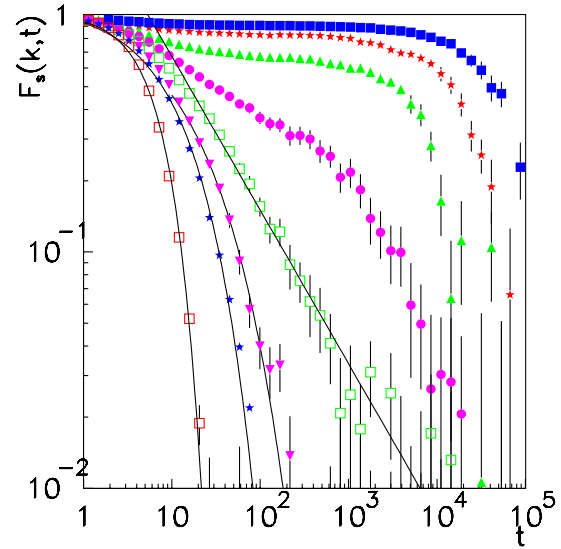


FIG. 2 (color online). $F_s(k, t)$ for $\phi = 0.02, 0.06, 0.07, 0.09, 0.10, 0.11, 0.12, 0.13$ (from left to right), and $k = k_{\min}$ as a function of t . The full lines are, from left to right, an exponential, a stretched ($\beta = 0.75 \pm 0.01$ and $\beta = 0.58 \pm 0.01$), and a power law $\sim t^{-c}$ with $c = 0.65 \pm 0.03$ (straight line).

$\chi_4(k, t) = N[\langle |\Phi_s(k, t)|^2 \rangle - \langle \Phi_s(k, t) \rangle^2]$. We argue that, for $k \rightarrow 0$ and $t \rightarrow \infty$, the dynamic susceptibility $\chi_4(k, t)$ tends to the mean cluster size. We define $\chi_{as}(k, \phi) \equiv \lim_{N \rightarrow \infty} \lim_{t \rightarrow \infty} \chi_4(k, t)$. Being $\lim_{t \rightarrow \infty} \langle \Phi_s(k, t) \rangle = 0$, we have

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

where $C_{ij}(k) = \lim_{t \rightarrow \infty} \langle e^{i\vec{k} \cdot [\vec{r}_i(t) - \vec{r}_j(t)]} e^{-i\vec{k} \cdot [\vec{r}_i(0) - \vec{r}_j(0)]} \rangle = \langle |e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)}|^2 \rangle$. Here we have used the fact that, for large enough time t , the term $e^{-i\vec{k} \cdot [\vec{r}_i(t) - \vec{r}_j(t)]}$ 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. We separate the sum over connected pairs ($\gamma_{ij} = 1$, i.e., pairs belonging to the same cluster) and disconnected pairs ($\gamma_{ij} = 0$, that is, pairs belonging to different clusters), so that:

$$\begin{aligned} \chi_{as}(k, \phi) &= \lim_{N \rightarrow \infty} \frac{1}{N} \left[\sum_{i,j=1}^N \gamma_{ij} C_{ij}(k) \right] \\ &+ \frac{1}{N} \left[\sum_{i,j=1}^N (1 - \gamma_{ij}) C_{ij}(k) \right]. \end{aligned} \quad (2)$$

If particles i and j are not connected, for any fixed value of $k > 0$, the quantity $C_{ij}(k)$ is $O(1/N^2)$ [16]. As there are at most N^2 disconnected pairs, the second term of the right-hand side of Eq. (2) 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 ξ , so that the relative distance $|\vec{r}_i - \vec{r}_j|$ of connected particles will be lower than ξ . Therefore, we have $\lim_{k \rightarrow 0} \gamma_{ij} C_{ij}(k) = \gamma_{ij}$, so that finally

$$\lim_{k \rightarrow 0} \chi_{as}(k, \phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \left[\sum_{i,j=1}^N \gamma_{ij} \right] = \chi, \quad (3)$$

where χ is the mean cluster size. The numerical data confirm this result. In Fig. 3 $\chi_4(k_{\min}, t)$ is plotted for $\phi \leq \phi_c$, while in the inset $\chi_{as}(k_{\min}, \phi)$, calculated as the long time limit of $\chi_4(k_{\min}, t)$, is plotted as a function of $(\phi_c - \phi)$ together with the mean cluster size. We have verified that $\chi_{as}(k, \phi)$ for $k = k_{\min}$ is equal to its $k \rightarrow 0$ limit. The data show that $\chi_{as}(k_{\min}, \phi)$ is equal, within the numerical errors, to the mean cluster size, diverging at the percolation threshold as a power law, with the same exponent γ of the mean cluster size.

Using a standard scaling argument [8], we can also predict the behavior of $\chi_{as}(k, \phi)$ for small k close to ϕ_c . In fact, $\chi_{as}(k, \phi) \sim (\phi_c - \phi)^{-\gamma}$ for $k = 0$, for finite small k , $\chi_{as}(k, \phi) \sim (\phi_c - \phi)^{-\gamma} g(k\xi)$, where $\xi = A(\phi_c - \phi)^{-\nu}$, and $g(z)$ is a function, which tends to a constant for small z , whereas it behaves as $z^{-\gamma/\nu}$ for large values of z [17]. Alternatively, starting from this scaling form, after simple algebra, we can also write $\chi_{as}(k, \phi) = k^{\eta-2} f(k\xi)$, where we have defined $2 - \eta = \gamma/\nu$ and $f(k\xi) = A^{-\gamma/\nu} (k\xi)^{\gamma/\nu} g(k\xi)$. Figure 4 shows that the numerical

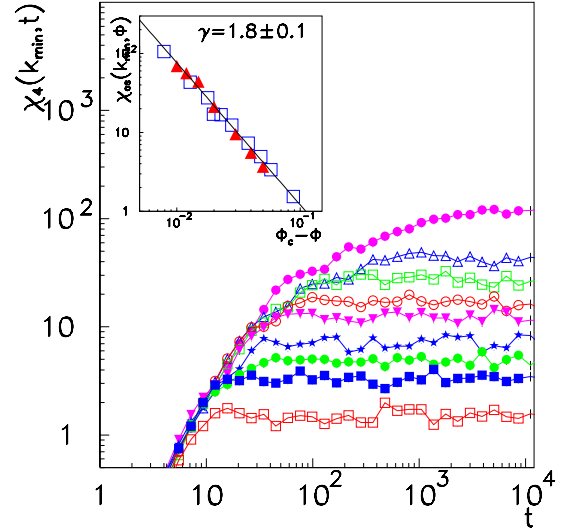


FIG. 3 (color online). Main frame: $\chi_4(k_{\min}, t)$ as a function of t for $\phi = 0.02, 0.05, 0.06, 0.07, 0.08, 0.085, 0.09, 0.095, 0.10$ (from bottom to top). Inset: asymptotic values of the susceptibility (\blacktriangle), $\chi_{as}(k_{\min}, \phi)$, and mean cluster size (\square) as a function of $(\phi_c - \phi)$. The data are fitted by the power law $(\phi_c - \phi)^{-\gamma}$ with $\gamma = 1.8 \pm 0.1$.

data strongly support this scaling behavior. A rescaling of data including time is also possible [14].

In conclusion, according to these results the percolation critical exponents in the sol-gel transition could be measured directly via the fluctuations of the self-ISF, without the manipulation of the sample needed in usual methods [11,18]. Moreover, our results confirm that one key difference between irreversible gelation due to chemical bonds

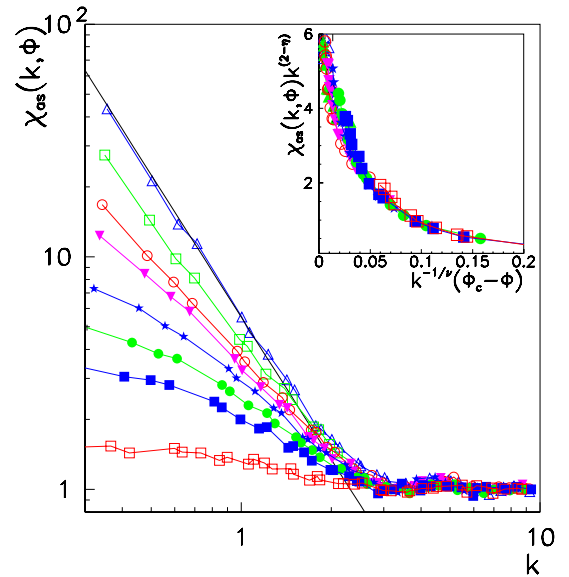


FIG. 4 (color online). Main frame: $\chi_{as}(k, \phi)$ as a function of the wave vector k and $\phi = 0.02, 0.05, 0.06, 0.07, 0.08, 0.085, 0.09, 0.095$ (from bottom to top). Close to ϕ_c the data are fitted by $k^{\eta-2}$ (full line), with $2 - \eta = 2.03 \pm 0.02$. Inset: scaling plot of $\chi_{as}(k, \phi) k^{2-\eta}$ as a function of $k^{-1/\nu} (\phi_c - \phi)$.

and supercooled liquids close to the glass transition is that in irreversible gelation the heterogeneities have a static nature (clusters). Interestingly, the behavior of the dynamic susceptibility is very similar to the one observed in spin glass models [19], where for long times it tends to the non linear static susceptibility, which diverges at the spin glass critical point.

Finally we suggest that our results may have strong implications in the study of colloidal gels, where bonds are not quenched and have a finite lifetime. We expect that, in attractive colloids at low temperature and volume fraction, the fluctuations of the self-ISF on a short time scale should probe the presence of clusters as if they were made of permanent bonds. The dynamic susceptibility as a function of time should therefore increase towards the mean cluster size. However, at longer times the number of bonds which survive is smaller, so the effective cluster size decreases resulting in a drop of the dynamic susceptibility. We therefore expect that the dynamic susceptibility reaches a maximum and then decreases. This is very similar to what is found in glass formers, except that, in colloidal gelation the dynamic heterogeneities are represented by the clusters made of long living bonds. And it is this difference in the dynamic heterogeneities, which may give rise, in such systems, to their peculiar dynamic behavior in part similar to gels with permanent bonds, and in part similar to glass formers.

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- [16] We can write

$$\langle e^{-i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)} \rangle = \frac{1}{N} \int d^3\vec{r} e^{-i\vec{k}\cdot\vec{r}} \rho[h_{ij}(\vec{r}) + 1], \quad (4)$$

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. For disconnected pairs, in the thermodynamic limit ($N \rightarrow \infty$ and $L \rightarrow \infty$ leaving the density ρ constant) the integral in Eq. (4) remains finite for any finite fixed k , so that the left-hand side of Eq. (4) is $O(1/N)$. In fact, the first term, the Fourier transform of the correlation function $h_{ij}(\vec{r})$, is finite when $L \rightarrow \infty$ since $h_{ij}(\vec{r})$ decays to zero at a finite distance. The second term, the modulus of the Fourier transform of 1, is not larger than $8/|k_x k_y k_z|$, and consequently remains finite when $L \rightarrow \infty$. The quantity $C_{ij}(k)$, being the square modulus of the left-hand side of Eq. (4), is therefore $O(1/N^2)$.

- [17] This scaling form stems from the scaling assumption that by rescaling all lengths by a factor λ : ξ/λ and λk , $\chi_{as}(k, \phi)$ must be rescaled by a factor λ^x , with $x = \gamma/\nu$ being fixed by the critical behavior at $k = 0$.
- [18] In usual approaches the sample needs to be dissolved in a known quantity of solvent in such a way that each cluster is separated from the others. The mean cluster size is then measured by light scattering. Beyond the gelation threshold, the finite clusters, which are trapped in the holes of the gel, must be extracted from the gel phase. Such separation of the sol and gel is very difficult to achieve experimentally, and the clusters in this process tend to break.
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