Static and dynamic heterogeneities in irreversible gels and colloidal gelation

Static and dynamic heterogeneities in irreversible gels and colloidal gelation

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

Dipartimento di Scienze Fisiche, Università degli Studi di Napoli 'Federico II', INFN, CNR-INFM Coherentia and CNISM, via Cinthia, 80126 Napoli, Italy

Abstract

We compare the slow dynamics of irreversible gels, colloidal gels, glasses and spin glasses by analysing the behaviour of the so-called nonlinear dynamical susceptibility, a quantity usually introduced to quantitatively characterize the dynamical heterogeneities. In glasses this quantity typically grows with time, reaches a maximum and then decreases at large times, due to the transient nature of dynamical heterogeneities and to the absence of a diverging static correlation length. We have recently shown that in irreversible gels the dynamical susceptibility is instead an increasing function of time, as in the case of spin glasses, and that it tends asymptotically to the mean cluster size. On the basis of molecular dynamics simulations, we show here that in colloidal gelation where clusters are not permanent, at very low temperature and volume fractions, i.e. when the lifetime of the bonds is much larger than the structural relaxation time, the nonlinear susceptibility has a behaviour similar to that of the irreversible gel, followed, at higher volume fractions, by a crossover towards the behaviour of glass-forming liquids.

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

1. Introduction

Many complex systems, such as glasses, spin glasses, irreversible gels, colloidal gels and others, exhibit a complex dynamics, all characterized by a slowing down usually leading to a structural arrest. Nevertheless there are significative differences among these systems, often not well clarified. One of the key concepts to describe the slow dynamics in glassy systems is that of dynamical heterogeneities. Here we want to classify and compare the above systems by looking at the behaviour of the so-called nonlinear dynamical susceptibility, a quantity usually introduced to quantitatively characterize the dynamical heterogeneities. In glass-forming liquids different definitions have been proposed for the nonlinear dynamical susceptibility [1, 2]. Mostly considered are the fluctuations of the self-intermediate and the total-intermediate scattering functions. These quantities typically have similar behaviour,

grow with time, reach a maximum and then decrease at large times. This behaviour is a consequence of the transient nature of dynamical heterogeneities and the absence of a diverging static correlation length. On the other hand, for systems with quenched interactions such as spin glasses, characterized by a diverging static correlation length at the spin glass critical temperature, the dynamical susceptibility defined as the fluctuations of the time-dependent spin–spin autocorrelation function is a monotonic function increasing with time. As the time goes to infinity this dynamical susceptibility for a fixed temperature T tends to a plateau whose value coincides with the static nonlinear susceptibility. Therefore as T approaches the spin glass temperature the value of the plateau diverges with the same behaviour as the static nonlinear susceptibility. In irreversible gels the definition of the corresponding dynamic susceptibility is not straightforward and one should carefully distinguish different dynamical quantities. We have recently shown [3] that in a microscopic model for irreversible gels the dynamical susceptibility defined as the fluctuations of the self-intermediate scattering function is a monotonic function as in the case of spin glasses and, for each fixed value of the volume fraction, its long-time limit tends to a plateau whose value coincides with the mean cluster size. The value of this plateau therefore diverges at the percolation threshold as the mean cluster size. Such a finding corresponds to the fact that in irreversible gelation the heterogeneities are due to the static nature of the clusters.

On this basis, we speculate that in colloidal gelation, where clusters are not permanent due to the finite bond lifetime, this nonlinear susceptibility should show a behaviour similar to the dynamical susceptibility of the irreversible gel at very low temperature and very low volume fraction, where the lifetime of the bonds is much larger than the structural relaxation time. At higher volume fractions and temperature, it should cross over towards a behaviour of glass-forming liquids. Here we give some evidence based on some molecular dynamics simulations of a model for colloidal gelation [4–6]. Moreover, using this scenario, we interpret previous results found in experimental investigations of colloidal suspension [7] and in some molecular dynamics simulations [4]. Finally, we also show that, in the spin glass type of model, when the lifetime of the interaction is made finite the behaviour found is similar to that found in colloidal systems [8].

In the following, first we recall the behaviour of linear dynamical susceptibility of glass-forming liquids and spin glasses (section 2.1). Then (section 2.2) we consider the case of irreversible gels. In section 3.1, we discuss the case of colloidal gelation and compare with a spin glass type of model with annealed interactions (section 3.2). Finally we analyse the emerging scenario and the further developments that this study suggests (section 4).

2. Systems with quenched interactions

2.1. Spin glasses

We briefly recall the 3d Ising spin glass where the Hamiltonian of the model is $H = J \sum_{\langle ij \rangle} \epsilon_{ij} S_i S_j$, with $S_i = \pm 1$ Ising spins, and $\epsilon_{ij} = \pm 1$ quenched and disordered interactions. The 3d model undergoes a transition at a temperature, T_{SG}, with a divergence of the static nonlinear susceptibility, $\chi_{nl} = \frac{1}{N} \sum_{ij} [\langle S_i S_j \rangle^2]$, where the average $\langle \cdots \rangle$ is over the Boltzmann measure, and the average $[\cdots]$ is over the disorder configurations. The dynamical nonlinear susceptibility was first introduced in p-spin models, considered as the prototype models of glass formers in mean field [1],

$$\chi(t) = N[\langle q(t)^2 \rangle - \langle q(t) \rangle^2], \tag{1}$$

where $q(t) = \frac{1}{N} \sum_i S_i(t') S_i(t' + t)$ and the average $\langle \cdots \rangle$ is done on the reference time t'. In the 3d Ising spin glass, differently from the behaviour observed in p-spin models, $\chi(t)$ grows

monotonically until a plateau value is reached. The plateau value coincides with the static nonlinear susceptibility and diverges at the transition [8].

2.2. Irreversible gels

In this section we present a molecular dynamics (MD) study of a microscopic model recently introduced [3] for irreversible gels. We consider a 3d system of $N = 1000$ particles interacting via a Lennard-Jones potential, truncated in order to have only the repulsive part:

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

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,

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

representing a finitely extendable nonlinear elastic (FENE) [9]. The system is then further thermalized. We have chosen $k_0 = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$ as in [9] 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 [10] 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 0.2. By varying the volume fraction we find that the system undergoes a percolation transition in the universality class of the random percolation. We have investigated the dynamical evolution of the system by studying the self-intermediate scattering functions, $\Phi_s(k, t) = \frac{1}{N}\sum_{i=1}^N e^{i\vec{k}\cdot(\vec{r}_i(t)-\vec{r}_i(0))}$, for increasing volume fractions. As it is found in experiments on real gels, we observe stretched exponential decays at volume fractions lower than the percolation threshold ϕ_c, and the onset of power law decays when ϕ approaches ϕ_c.

We have moreover measured the dynamical susceptibility associated to the fluctuations of the self-intermediate scattering functions [2], i.e. $\chi_4(k, t) = N[\langle|\Phi_s(k, t)|^2\rangle - \langle\Phi_s(k, t)\rangle^2]$, where $\langle\cdots\rangle$ is the thermal average for a fixed bond configuration and $[\cdots]$ is the average over the bond configurations. We have shown analytically in [3] that this quantity, in the thermodynamic limit, for $t \to \infty$ and $k \to 0$, tends to the mean cluster size.

In the main frame of figure 1, $\chi_4(k_{\min}, t)$ (with $k_{\min} = 2\pi/L$) is plotted for increasing values of the volume fractions $\phi \leqslant \phi_c$. In contrast to the non-monotonic behaviour typically observed in glassy systems, we find that it increases with time until it reaches a plateau, whose value increases as a function of ϕ.

In the inset of figure 1, $\chi_{as}(k_{\min}, \phi) \equiv \lim_{t\to\infty} \chi_4(k_{\min}, t)$ 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, $\chi_{as}(k_{\min}, \phi)$ diverges as a power law at ϕ_c. The exponent, within numerical accuracy, is in agreement with the value of the exponent γ of the mean cluster size. This finding confirms that one key difference between irreversible gelation due to chemical bonds and supercooled liquids close to the glass transition is that in irreversible gelation the heterogeneities have a static nature (clusters). The 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).
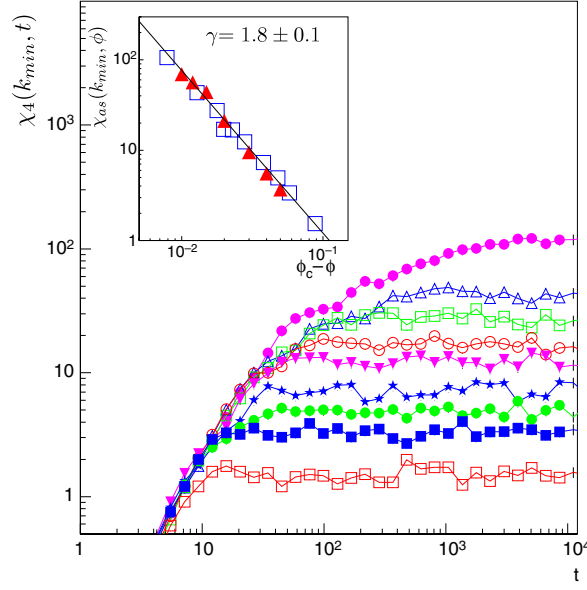
Figure 1. Main frame: $\chi_4(k_{\min}, t)$ as a function of t for $\phi = 0.02, 0.05, 0.06, 0.07, 0.08, 0.085,$ $0.09, 0.095, 0.10$ (from bottom to top). Inset: asymptotic values of the susceptibility (full triangles), $\chi_{as}(k_{\min}, \phi)$ and mean cluster size (open squares) as a function of $(\phi_c - \phi)$. The data are fitted by the power law $(\phi_c - \phi)^{-\gamma}$ with $\gamma = 1.8 \pm 0.1$.

The behaviour observed in the case of permanent gels is very similar to that of spin glasses in finite dimensions. Although these systems have very different structures, they show a very similar dynamical behaviour due to the static nature of heterogeneities. In both cases interactions are quenched. What can we expect in the cases where the interactions are not quenched and have a finite lifetime? In the following section we will try to answer this question.

3. Systems with finite bond lifetime

3.1. Colloidal gelation

In this section we present the results obtained in an MD study of a DLVO (Derjaguin, Landau, Verwey and Overbeck)-type potential [11] for charged colloidal systems, and discuss how in colloidal gelation the finite bond lifetime affects the dynamics and, in particular, the behaviour of the dynamical susceptibility.

We consider a system of $N = 10\,000\,\phi$ particles, interacting via a potential which contains a van der Waals type interaction plus an effective repulsion due to the presence of charges:

$$V(r) = \epsilon \left[a_1 \left(\frac{\sigma}{r} \right)^{36} - a_2 \left(\frac{\sigma}{r} \right)^6 + a_3 e^{-\lambda \left(\frac{r}{\sigma} - 1 \right)} \right], \tag{2}$$

where $a_1 = 2.3$, $a_2 = 6$, $a_3 = 3.5$, and $\lambda = 2.5$. With these parameters the repulsion term dominates the van der Waals attraction at long range, providing a short-range attraction and a long-range repulsive barrier. The potential is truncated and shifted at a distance of 3.5σ. To mimic the colloidal dynamics, we performed MD simulations at constant temperature. Equations of motion were solved in the canonical ensemble (with a Nosé–Hoover thermostat) using a velocity Verlet algorithm with a time step of $0.001t_0$ (where $t_0 = \sqrt{\frac{m\sigma^2}{\epsilon}}$ and m is the mass of the particles).
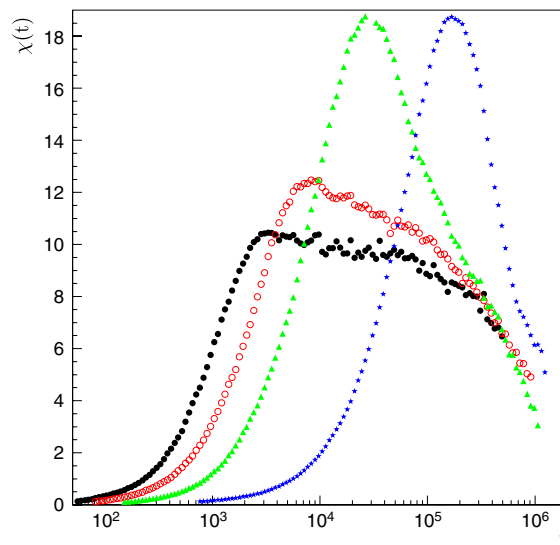
Figure 2. The dynamic susceptibility, $\chi_4(k_{\min}, t)$, for $k_B T = 0.15\epsilon$ and $\phi = 0.10, 0.11, 0.12, 0.13$ (from left to right).

We find [4–6] that at low volume fraction compact stable clusters form with typical size $s \simeq 10$. By increasing the volume fraction a residual attractive interaction between the clusters produces elongated structures, which finally order in a columnar phase [5]. A small degree of polydispersity is introduced [6] in order to avoid the transition to the ordered phase. In this case, by increasing the volume fraction the elongated structures form instead a long-living random percolating network, i.e. the gel phase. The bond lifetime has a non-monotonic behaviour. At $k_B T = 0.15\epsilon$ it decreases by about one order of magnitude from $\phi = 0.10$ to 0.13, has a minimum at 0.13, and finally increases for $\phi > 0.13$.

The dynamical susceptibility, $\chi_4(k_{\min}, t)$, is measured for $\phi = 0.10, 0.11, 0.12, 0.13$ (see figure 2). The data give evidence of a clear crossover from the low volume fraction regime to the intermediate regime. In the first regime, where the bond lifetime is much larger than the structural relaxation time, we find a behaviour resembling that observed in the permanent gels. Although $\chi_4(k_{\min}, t)$ is a non-monotonic function, it increases until a value comparable to the mean cluster size is reached; a plateau decreasing slowly as a function of time is clearly present in the intermediate time region; finally, at very long times, $\chi_4(k_{\min}, t)$ decreases to its equilibrium value. Increasing ϕ, the bond lifetime and the structural relaxation time become comparable. In this case $\chi_4(k_{\min}, t)$, which is again a non-monotonic function, displays a well-pronounced maximum as usually observed in glassy systems. These data suggest that in the first regime the clusters behave dynamically as being made of permanent bonds, as in chemical gelation, and the dynamics is dominated by the presence of such clusters. On increasing ϕ, the structural relaxation begins to be affected also by the crowding of the particles, and a clear crossover to a new glassy regime is found.

3.2. A spin glass type of model with annealed interactions

It is now extremely interesting to analyse the case of annealed interactions in a spin glass type of model. To this aim we consider the results obtained in Monte Carlo simulations of the so-called frustrated lattice gas (FLG). This model, recently introduced in connection with the glass
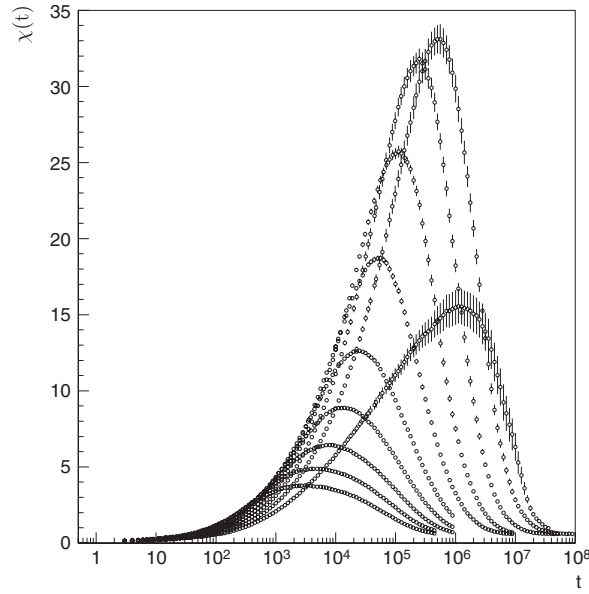
Figure 3. Dynamical nonlinear susceptibility in the annealed FLG for densities $\rho = 0.52, 0.53,$ 0.54, 0.55, 0.56, 0.57, 0.58, 0.59, 0.60, 0.61 (from left to right).

transition [12, 13], has mean-field properties closely related to those of p-spin models. Being constituted by diffusing particles, it is suited to study quantities like the diffusion coefficient, or the density autocorrelation functions, that are usually important in the study of liquids. The Hamiltonian of the model is

$$-\beta H = J \sum_{\langle ij \rangle} (\epsilon_{ij} S_i S_j - 1) n_i n_j + \mu \sum_i n_i, \tag{3}$$

where $S_i = \pm 1$ are Ising spins, $n_i = 0, 1$ are occupation variables, and $\epsilon_{ij} = \pm 1$. In the case where ϵ_{ij} are quenched variables randomly distributed, the 3d model undergoes a transition of the type of 3d spin glasses [14]. Here we considered the case where the interactions ϵ_{ij} evolve in time, i.e. they are annealed variables [8]. In this case dynamical properties strongly resembling those of glass formers and well fitted by the mode coupling theory for supercooled liquids are found.

The dynamical nonlinear susceptibility is defined by

$$\chi(t) = N[\langle q(t)^2 \rangle - \langle q(t) \rangle^2], \tag{4}$$

where $q(t) = \frac{1}{N} \sum_i S_i(t') n_i(t') S_i(t'+t) n_i(t'+t)$ and the average $\langle \cdots \rangle$ is done on the reference time t'. In figure 3, $\chi(t)$ is plotted for increasing values of the density. The same behaviour of the p-spin model in mean field [1] and of MD simulations of the Lennard-Jones binary mixture [15] is observed: $\chi(t)$ shows a maximum, $\chi(t^*)$, at a time t^*, and both $\chi(t^*)$ and t^* seem to diverge when the density grows. For the highest density, the maximum of $\chi(t)$ decreases, possibly due to the transition to an unfrustrated state. Comparing the behaviour found in this case with that shown in the previous section, we note that here the first regime with a clear plateau in the susceptibility is not present. This is probably due to the fact that the interaction relaxation time is in this case always comparable to the structural relaxation time.

4. Conclusions

By means of the dynamical susceptibility, we have here analysed the presence of dynamical heterogeneities in systems with quenched and annealed interactions. In the case of quenched interactions, as happens in spin glasses, the dynamical susceptibility grows monotonically in time until a plateau value is reached. The plateau value coincides with the static nonlinear susceptibility and diverges at the transition. This behaviour is in fact also observed in a microscopic model for irreversible gels, where the plateau value of the dynamic susceptibility diverges at the percolation transition as the mean cluster size. These results confirm that in irreversible 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).

With annealed interactions instead, in the case of spin glass type of models, one recovers the non-monotonic behaviour of the dynamical susceptibility, which is typically observed in glasses. This is due to the transient nature of dynamical heterogeneities and the absence of a diverging static correlation length. We analyse moreover the case of colloidal gelation, where the clusters are not permanent due to the finite lifetime of the bonds. We find that the dynamical susceptibility is again a non-monotonic function, and displays at high volume fraction a well-pronounced maximum as usually observed in glassy systems. Remarkably, at very low temperature and very low volume fraction, where the lifetime of the bonds is much larger than the structural relaxation time, the dynamical susceptibility shows a behaviour similar to the dynamical susceptibility of the irreversible gel with a crossover, at higher volume fractions, towards a behaviour typical of glass-forming liquids. These results suggest that in the first regime the dynamics is dominated by clusters, made of bonds which can be considered as permanent in this time window. On increasing ϕ, when these two timescales become comparable, the structural relaxation begins to be affected also by the crowding of the particles, and a clear crossover to a new glassy regime is found.

References

[1] Franz S, Donati C, Parisi G and Glotzer S C 1999 *Phil. Mag.* B **79** 1827
    Donati C, Glotzer S C, Poole P H, Kob W and Plimpton S J 1999 *Phys. Rev.* E **60** 3107
[2] Bouchaud J P and Biroli G 2005 *Phys. Rev.* B **72** 064204
    Toninelli C, Biroli G and Fisher D S 2006 *Phys. Rev. Lett.* **96** 035702
[3] Abete T, de Candia A, Del Gado E, Fierro A and Coniglio A 2007 *Preprint* cond-mat/0607815
[4] Coniglio A, de Arcangelis L, Del Gado E, Fierro A and Sator N 2004 *J. Phys.: Condens. Matter* **16** S4831
    de Candia A, Del Gado E, Fierro A, Sator N and Coniglio A 2005 *Physica* A **358** 239–48
[5] de Candia A, Del Gado E, Fierro A, Sator N, Tarzia M and Coniglio A 2006 *Phys. Rev.* E **74** 010403
[6] de Candia A, Del Gado E, Fierro A and Coniglio A, 2007 in preparation
[7] Cipelletti L and Ramos L 2005 *J. Phys.: Condens. Matter* **17** R253
    Duri A, Bissig H, Trappe V and Cipelletti L 2005 *Phys. Rev.* E **72** 051401
    Duri A and Cipelletti L 2006 *Europhys. Lett.* **76** 972
[8] Fierro A, de Candia A and Coniglio A 2001 *Phys. Rev.* E **62** 7715
    Fierro A 2004 *Phys. Rev.* E **70** 012501

[9]   Grest G S and Kremer K 1986 *Phys. Rev.* A **33** 3628
       Kremer K and Grest G S 1990 *J. Chem. Phys.* **92** 5057
[10] Allen M P and Tildsley D J 2000 *Computer Simulation of Liquids* (Oxford: Oxford Press)
[11] Israelachvili J N 1985 *Intermolecular and Surface Forces* (London: Academic)
       Crocker J C and Grier D G 1994 *Phys. Rev. Lett.* **73** 352
[12] Coniglio A, Frustration and connectivity in glass forming systems and granular materials *Proc. Int. School on the
       Physics of Complex Systems 'Enrico Fermi' CXXXIV Course (Varenna 1996)* ed F Mallamace and
       H E Stanley, p 491
       Coniglio A, de Candia A, Fierro A and Nicodemi M 1999 *J. Phys.: Condens. Matter* **11** A167
       Ricci-Tersenghi F, Stariolo D A and Arenzon J 2000 *Phys. Rev. Lett.* **84** 4473
       Vainstein M H, Stariolo D A and Arenzon J J 2003 *J. Phys. A: Math. Gen.* **36** 10907
[13] Arenzon J J, Nicodemi M and Sellitto M 1996 *J. Physique* I **6** 1143
       Sellitto M, Nicodemi M and Arenzon J J 1997 *J. Physique* I **7** 945
       Crisanti A and Leuzzi L 2002 *Phys. Rev. Lett.* **89** 237204
       Crisanti A and Leuzzi L 2004 *Phys. Rev.* B **70** 014409
[14] de Candia A and Coniglio A 2002 *Phys. Rev.* E **65** 16132
[15] Glotzer S C, Novikov V N and Schrøder T B 2000 *J. Chem. Phys.* **112** 509