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Abstract
We propose a simple statistical mechanics model for the study of the dynamics of gelling systems. It is based on percolation and bond-fluctuation dynamics for the bond vectors: we study the critical viscoelastic properties and the relaxation patterns in the case of irreversible gelation and the results obtained are discussed by means of scaling arguments. By introducing the idea of a finite lifetime for the bonds and by simply tuning this timescale, the model can be made to present very different dynamics and relaxation patterns corresponding to different gelling phenomenology.

1. Introduction

There is a growing interest in studying gelling systems such as polymers, colloids, and biological systems. These are systems undergoing a dynamical transition which transforms the material from a viscous liquid to an elastic solid [1–3]. It is a transition between two different viscoelastic regimes and it is essentially characterized by the critical behaviour of the viscosity coefficient and the elastic modulus, and by a complex non-exponential relaxation behaviour. This dynamical transition corresponds to the constitution of a macromolecular structure, the gel phase, and some aspects of the transition have been investigated in depth by means of percolation models. There are also some interesting analogies with the dynamics at the glass transition, but here the relaxation process and the dramatic change in the viscoelastic properties are actually controlled by the growth of the connectivity. These features are actually common to all gelling systems and to some extent unify their phenomenology. Moreover, it has been recently suggested [4] that the different and puzzling phenomena of the glass transition, gelation, and aggregation in colloids may be unified in a common jamming phase diagram, i.e. they can be interpreted as different aspects of a unique jamming transition as long as an interconnected stress-bearing network is present in the system. This idea is supported in colloids by the observation of the same characteristic critical behaviour of the viscoelastic properties. In spite of this, the relaxation properties show a variety of complex behaviours

depending on the type of the material [5]. Moreover, for the critical behaviour of the viscosity and elasticity, the experimental data are rather scattered and different theoretical models give different predictions.

Thus, the problem is to understand how the essential features of the gelation transition and of the typical gelling system may produce this variety of phenomenological behaviours. Our approach is to build up a simple statistical mechanics model to enable us to directly link the dynamical behaviours to the fundamental elements of the model.

We study the dynamics at the gelation transition with a model based on percolation and a suited dynamics for percolation clusters. In the case of permanent bonds, a permanent interconnected network, i.e. a static percolating cluster, is present in the gel phase. Within a viscoelasticity approach, the dynamics of the system can be described in terms of characteristic relaxation times; for example, in the sol phase the viscosity coefficient diverging as the percolation threshold is approached corresponds to a diverging average relaxation time. Permanent bonds correspond then to interactions between monomers that do not change within the observation timescale. In this sense the interconnected stress-bearing network formed at the percolation threshold is permanent, as it is not locally changed on any timescale considered. If bonds change on timescales comparable to or smaller than the observation timescale and the average relaxation time linked to the diffusion of the clusters, one has a gel phase which is characterized by a dynamically evolving percolating structure. This possibility can be simply reproduced in our model by opportunely changing the fundamental parameters, and in preliminary studies we observe a striking change in the dynamics and the relaxation patterns. On the whole, the results suggest that this could be a unifying model for the study of the phenomenology of gelling systems. In section 2 the model is presented. In section 3 the results obtained via numerical simulations are given and discussed. Section 4 contains concluding remarks and perspectives.

2. Model and numerical simulations

Our model introduces, within the random-percolation model, bond-fluctuation (BF) dynamics, which is able to take into account the polymer conformational changes [6]. We study a solution of tetrafunctional monomers at concentration p and with a probability p_b of bond formation. In terms of these two parameters, one has different cluster size distributions and eventually a percolation transition. The monomer diffusion process produces a variation of the bond vectors and is constrained by the excluded-volume interaction and the SAW condition for polymer clusters: these two requirements can be satisfied if the bond lengths vary within the allowed range. The gel phase and the corresponding dynamic transition correspond to the construction of a percolating network. We can introduce the idea of finite bond lifetime τ_b: when it is smaller than the observation timescale and the average relaxation time linked to the cluster diffusion, one has a gel phase which is characterized by a dynamically evolving percolating structure. We have performed numerical simulations of this model on hypercubic lattices [7–9]. The BF dynamics can be easily expressed in a lattice algorithm: a monomer occupies a lattice elementary cell, two occupied cells cannot have common sites, and the dynamics constraints produce a finite set of allowed bond lengths corresponding to a large number of different bond vectors.

We have considered lattices of size L ranging between 16 and 40 in 3D with periodic boundary conditions: the eight sites which are the vertices of a lattice elementary cell are simultaneously occupied by a monomer, with the constraint that two nearest-neighbour (nn) monomers are always separated by an empty elementary cell, i.e. two occupied cells cannot have common sites. The lattice of cells, with double lattice spacing, has been occupied
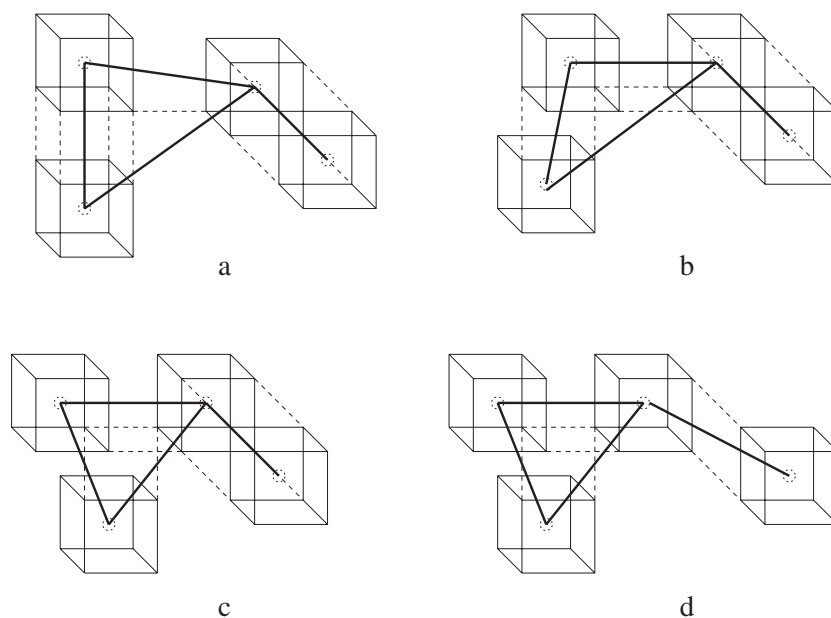
Figure 1. An example of time evolution of a cluster formed by four monomers according to the BF dynamics: in (a), starting from the upper central bond and clockwise, the bond lengths are $l = \sqrt{5}, 3, 3, 2$; in (b) the upper left monomer has moved forward and $l = 2, 3, 3, \sqrt{5}$; having moved the other remaining monomer in (b) to the right, one obtains (c) with $l = 2, 3, \sqrt{6}, \sqrt{6}$; moving the front monomer in (c) to the right, the (d) configuration is obtained with $l = 2, \sqrt{10}, \sqrt{6}, \sqrt{6}$.

with probability p, which coincides with the monomer concentration on the main lattice in the thermodynamic limit. Monomers are randomly distributed on the main lattice via a diffusion process; then between two nn or next-nearest-neighbour (nnn) monomers, bonds are instantaneously created with probability p_b along lattice directions. Since most of the experimental data on the gelation transition refer to polymers with monomer functionality $f = 4$, we have considered this case allowing the formation of at most four bonds per monomer. We let the system evolve according to the BF dynamics via the monomer movements (figure 1), and in the case of finite bond lifetime depending on the τ_b, the bonds are broken and formed.

All the data have been averaged over a sample of ~ 30 systems with different initial site and bond configurations. The numerical simulations have been performed on the CRAY-T3E system of CINECA.

3. Viscoelastic properties and relaxation behaviour

In the case of permanent bonds the model reproduces well the phenomenology of irreversible gelling systems. The diffusion behaviour of clusters in the sol at the percolation threshold shows a scaling behaviour for the diffusion coefficient D as a function of the cluster radius R (figure 2). This result can be interpreted by means of the following scaling argument: the generic probe of size R diffuses in a medium with a viscosity coefficient depending on R, $\eta(R)$, and a Stokes–Einstein *generalized* relation $D(R) \simeq 1/R^{d-2}\eta(R)$ should be expected to hold as long as the cluster radius is much greater than the value of the percolation correlation length. At the percolation threshold, the viscosity coefficient of the sol (the *bulk* viscosity coefficient) diverges as $\eta \sim (p_c - p)^{-k}$, and because of the self-similarity features of the
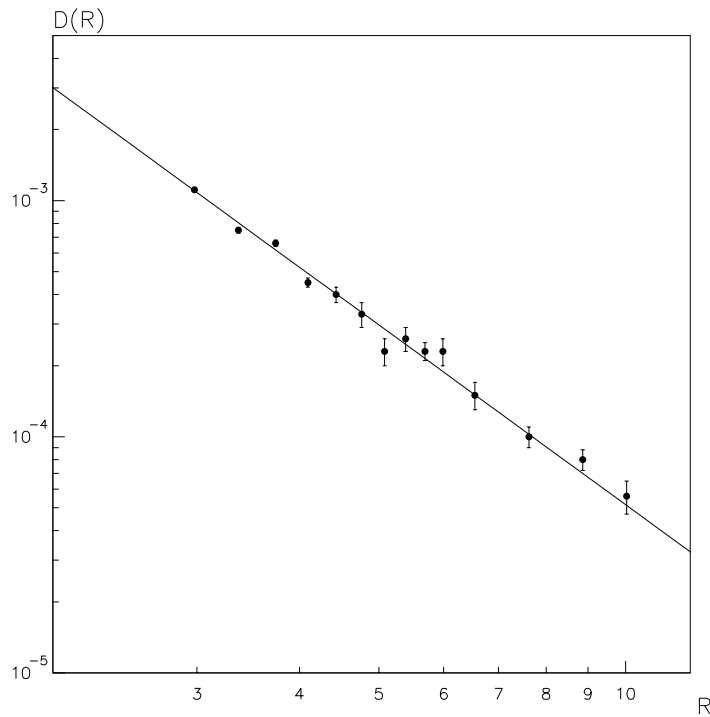
Figure 2. The diffusion coefficient at p_c averaged over 32 different configurations for different cluster sizes as a function of the cluster radius of gyration R.

percolating cluster the scaling behaviour is obtained:

$$D(R) \sim \frac{1}{R^{d-2+k/\nu}} \qquad (1)$$

at $p = p_c$ [7].

Following this argument, we obtain for the viscosity coefficient a critical exponent $k \sim 1.3 \pm 0.1$. In order to study the relaxation times in the system independently, we have calculated the time-autocorrelation function $g(t)$ of the number of pairs of nn monomers $\varepsilon(t)$, defined as

$$g(t) = \frac{\langle \varepsilon(t')\varepsilon(t'+t) \rangle - \langle \varepsilon(t') \rangle^2}{\langle \varepsilon(t')^2 \rangle - \langle \varepsilon(t')^2 \rangle} \qquad (2)$$

where $\langle \cdots \rangle$ indicates the average over t' (of the order of 10^3 time intervals). At different p-values in the critical region after a fast transient, $g(t)$ decays to zero but cannot be fitted by a simple time exponential behaviour (figure 3). This is a sign of the existence of a distribution of relaxation times which cannot be related to a single time. It is a typical feature of polymeric systems where the relaxation process always involves the rearrangement of the system over many different length scales [3, 11]. This idea of a complex relaxation behaviour is further confirmed by the good fit of the long-time decay of $g(t)$ with a stretched-exponential law [7]. This behaviour of the relaxation functions is considered typical of complex materials and usually interpreted in terms of a very broad distribution of relaxation times or eventually an infinite number of them, and it is in fact experimentally observed in a sol in the gelation
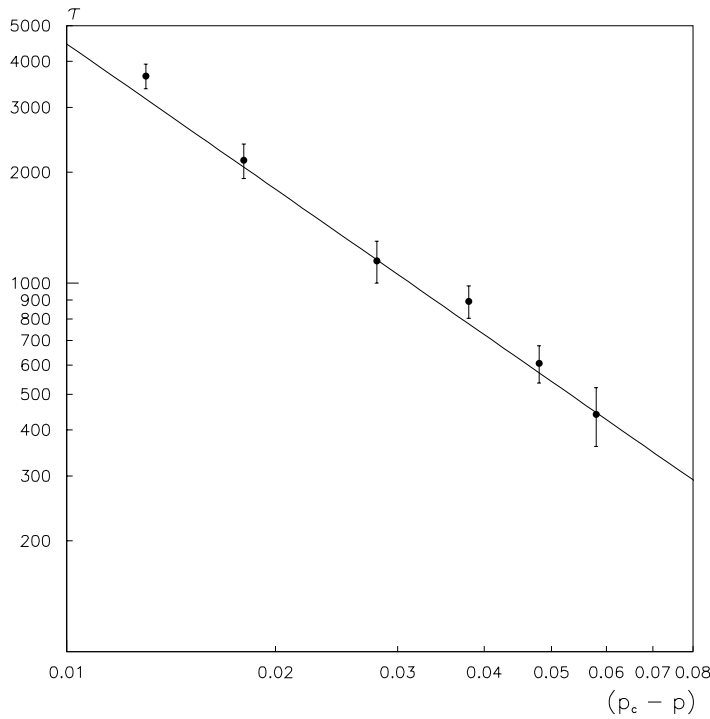
Figure 3. The characteristic integral time τ calculated according to equation (3) as a function of $(p_c - p)$. The data are fitted well by a power law with a critical exponent $k \sim 1.31 \pm 0.05$.

critical regime [5]. We then studied the average characteristic time defined as

$$\tau(p) = \frac{\int_0^t t' g(t') \, \mathrm{d}t'}{\int_0^t g(t') \, \mathrm{d}t'} \tag{3}$$

which is a typical macroscopic relaxation time and can be directly linked to the viscosity coefficient. Numerically, in equation (3), t has been chosen by the condition $g(t') \leqslant 0.001$ for $t' \geqslant t$.

For the irreversible gelling system, i.e. in the system with permanent bonds, this characteristic time grows with p and diverges at the percolation threshold according to the critical behaviour

$$\tau \propto (p_c - p)^{-k} \tag{4}$$

with an exponent $k \simeq 1.3 \pm 0.03$, which gives a critical exponent for the viscosity at the sol–gel transition in agreement with the result obtained from the diffusion properties of clusters [7]. This value of the critical exponent also agrees with the prediction based on the Rouse model and with some experimental data [10].

The elastic response in the gel phase is studied in terms of the macroscopic elastic constant of the system K, which is experimentally defined as the ratio between an applied external force and the deformation. In a simple elongation experiment, if l_0 is the undeformed length and $\delta = (l - l_0)$ is the deformation in the system, within the linear response approximation the elastic free energy $F \sim K\delta^2$. In terms of the Young elastic modulus E, the free energy per unit volume is $F/V \sim E\delta^2/l_0^2$. Then $K \sim EV/l_0^2$ and, for a cube of size L, $K \sim EL^{d-2}$,
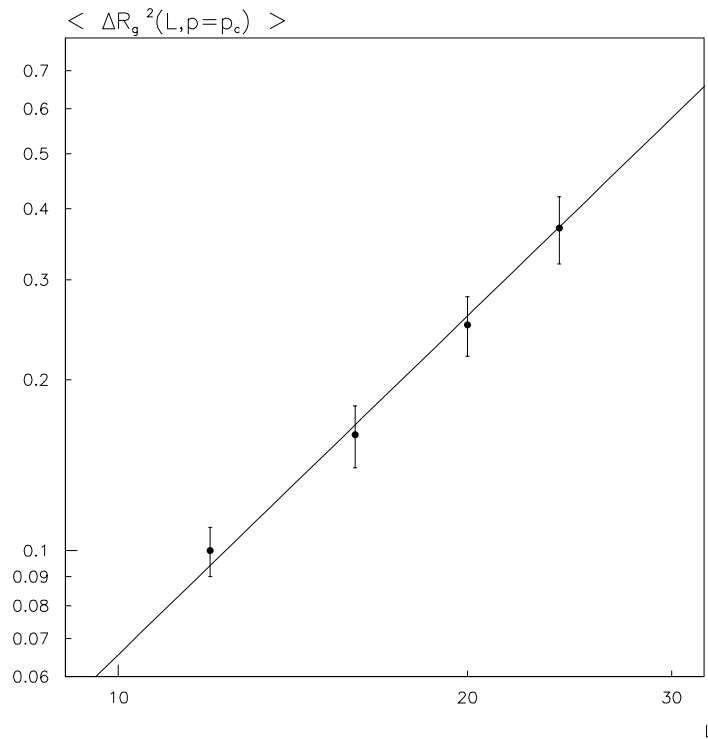
Figure 4. A log–log plot of the fluctuation of the percolating cluster gyration radius $\langle \Delta R_g^2 \rangle$ as a function of the lattice size L at p_c: from the fit of the data, the critical exponent $\tilde{z} \sim 1.9 \pm 0.1$ is obtained. The lengths are expressed in units of the lattice spacing.

expressing the fact that the elastic modulus has the dimensions of an energy per unit volume and is an intensive quantity, whereas K depends on the system size L.

In the gel, since E vanishes at p_c as $\sim \xi^{-\tilde{f}}$ (where $\tilde{f} = f/\nu$) one has $K \sim L^{d-2}\xi^{-\tilde{f}}$. As a consequence, for $p > p_c$ the macroscopic elastic constant $K \sim L^{d-2}$, whereas for $p = p_c$ the critical behaviour $K \sim L^{-\tilde{z}}$ is obtained, with $\tilde{z} = \tilde{f} - (d - 2)$.

On the other hand, for a fixed L and close to the percolation threshold, $K \sim (p - p_c)^f$.

The fluctuation-dissipation theorem relates the deformation in the linear size of the gel macromolecule δR—and so also the elastic response by means of the Hooke elastic constant K—to the time-autocorrelation function $\langle \delta R^2 \rangle$ in the unperturbed system. In fact, in the undeformed equilibrium system in the thermal bath at temperature T, the average fluctuation of the free energy is

$$\langle \Delta F \rangle = \tfrac{1}{2} K \langle \Delta R_g^2 \rangle \tag{5}$$

and is of the order of $k_B T$, so $K \sim 1\langle \Delta R_g^2 \rangle /$. The radius of gyration R_g is the average linear size of the gel macromolecule and $\langle \Delta R_g^2 \rangle = \langle (R_g - \langle R_g \rangle)^2 \rangle$.

We then calculated the average fluctuation in the gyration radius $\langle \Delta R_g^2 \rangle$ of the percolating cluster at the percolation threshold in systems of different sizes L. In figure 2 $\langle \Delta R_g^2 \rangle$ is shown in a log–log plot as a function of the lattice size L at p_c. In the range considered, the data are fitted well by a power-law behaviour, giving a critical exponent $\tilde{z} \sim 1.9 \pm 0.1$, i.e. $z \sim 1.7 \pm 0.1$. As $\tilde{z} = \tilde{f} - (d - 2)$, we have $f = z + (d - 2)\nu$, and this result gives $f \sim 2.6 \pm 0.1$.

This value is in good agreement with the prediction $f = d\nu$ of [12] and with the value observed experimentally in [13].

The study of the dynamic structure factor in the system shows the typical non-exponential relaxation patterns of irreversible gelling systems: a long-time stretched-exponential decay in the sol as the gel point is approached, where the occurrence of a power law is observed which also persists in the gel phase [9]—as is actually observed in experiments [5]. For the system with finite bond lifetime $\tau_b \neq \infty$, preliminary results show that the characteristic time τ grows with p approaching the corresponding value of the percolation threshold, but then τ has a finite jump and seems to go to a constant value. This finite jump in the viscosity coefficient is typically observed in aggregation phenomena in colloids [14]. Moreover, different relaxation patterns are observed in study of the dynamic structure factor [9].

4. Conclusions

Our model for the study of the dynamics of gelling systems is based on percolation and the BF dynamics. In the case of permanent bonds we have obtained the critical behaviour of the viscoelastic properties, in agreement with some experimental findings and some theoretical predictions, and the typical stretched-exponential and power-law relaxation patterns of irreversibly gelling systems. By introducing a finite lifetime for bonds, we preliminarily observe different dynamics and relaxation patterns, characterized by a finite jump in the viscosity coefficient, which is typically observed in aggregation phenomena. These results suggest that this could be a unifying model in the study of the phenomenology of gelling systems.

Acknowledgments

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