Viscosity critical behaviour at the gel point in a 3d lattice model

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Abstract

Within a recently introduced model based on the bond-fluctuation dynamics we study the viscoelastic behaviour of a polymer solution at the gelation threshold. We here present the results of the numerical simulation of the model on a cubic lattice: the percolation transition, the diffusion properties and the time autocorrelation functions have been studied. From both the diffusion coefficients and the relaxation times critical behaviour a critical exponent $k$ for the viscosity coefficient has been extracted: the two results are comparable within the errors giving $k \sim 1.3$, in close agreement with the Rouse model prediction and with some experimental results. In the critical region below the transition threshold the time autocorrelation functions show a long time tail which is well fitted by a stretched exponential decay.

PACS: 05.20.-y, 82.70.Gg, 83.10.Nn
Polymeric materials are characterized by a rich and complex phenomenology, which goes from non-newtonian dynamic behaviour in polymer liquids to viscoelastic properties of polymer gels and the glass transition of polymer melts, intensively investigated in the last decades. The interest in such systems has been recently further increased by several possibilities of technological applications in many different fields but still the non-trivial viscoelastic behaviour of polymeric systems does not have a completely satisfying description. The gelation transition which transforms the polymeric solution, i.e. the sol, in a polymeric gel is characterized by a dramatic change in the viscoelastic properties: this is usually described in terms of the divergence of the viscosity coefficient and the appearance of an elastic modulus which characterizes the gel phase \[ \beta \]. In the experiments both the viscosity coefficient and the elastic modulus dependence on the polymerization reaction extent are well fitted by a power law but the experimental determination of these critical exponents is quite controversial: the results are in fact scattered, probably because of the practical difficulties in obtaining the gelation transition in a reproducible manner, and could only be interpreted on the basis of a better comprehension of the relevant mechanisms in the transition. Recent experimental measurements of the viscosity critical exponent \( k \) give values ranging from 0.7 in diisocyanate/triol to 1.5 in epoxy resins whereas for the elastic modulus critical exponent \( t \) the values are even more scattered, ranging from 1.9 in diisocyanate/triol to 3.0 in polyesters (see references \[3–10\]).

With simple statistical mechanics models it is possible to analyse the essential aspects of the transition and its critical properties. From the Flory model this has led to the description of the gelation process in terms of a percolation transition. The percolation model has turned out to be the satisfactory model for the sol-gel transition \[11,12\], it is able to describe the role of connectivity and gives the critical exponents for all the geometrical properties, which are in perfect agreement with the experimental results. On the other hand the viscoelastic dynamic behaviour is not simply obtained in terms of the connectivity transition. The difficulties in studying the viscosity critical behaviour at the gel point come from the determination of the viscosity of a very complex medium, which is the sol at the transition...
threshold, a highly polydisperse polymeric solution at high concentration. The complex polymer dynamics is characterized by the relaxation processes over many different time scales and compete with the increasing connectivity to produce the observed viscoelastic behaviour. The simplest approach consists in considering the sol as a polydisperse suspension of solid spheres neglecting the cluster-cluster interactions and generalizing the Einstein formula for the viscosity of a monodisperse suspension of solid spheres [11], which corresponds to a highly diluted regime. Within the Flory classical theory of gelation the viscosity remains finite [1] or diverges at most logarithmically. Using instead the Rouse model for the polymer dynamics [13], which neglects the entanglement effects and the hydrodynamics interactions, the viscosity in a solution of polymeric clusters, expressed in terms of the macroscopic relaxation time, grows like $< R^2 >$ as the cluster radius $R$ grows in the gelation process. The contribution of the $n_s$ molecules of size $s$ and gyration radius $R_s$ to the average $<>$ is of the order of $s n_s R_s^2$ leading to the critical exponent $k = 2\nu - \beta$ [14], where $\nu$ is the critical exponent of the correlation length diverging at the gel point and $\beta$ is the critical exponent describing the growth of the gel phase. With the random percolation exponents the value $k \sim 1.35$ is found, that agrees quite well with the experimental measurements for silica gels of ref. [6,7]. Actually this Rouse exponent could be considered as an upper limit due to the complete screening of the hydrodynamic interactions and the entanglement effects. The Zimm approach [13], where the monomer correlation due to the hydrodynamic interactions are not completely screened, would give a smaller exponent.

Another approach has been proposed by de Gennes [14] using an analogy between the viscosity at the gelation threshold and the diverging conductivity in the random superconducting network model. Following this analogy an exponent $k \sim 0.7$ is obtained in $3d$, according to the determination of the conductivity critical exponent in the random superconducting model [15]. This result is in good agreement with the values experimentally obtained in gelling solutions of polystyrene/divinylbenzene and diisocyanate/triol [14].

Our approach consists in directly investigating the viscoelastic properties at the sol-gel transition, introducing within the random percolation model the bond fluctuation (BF) dynam-
ics which is able to take into account the polymer conformational changes \cite{16,17}. We study a solution of tetrafunctional monomers at concentration $p$ and with a probability $p_b$ of bonds formation. In terms of these two parameters one has different cluster size distributions and eventually a percolation transition. Monomers interact via excluded volume interactions and can diffuse with local random movements. 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 an allowed range. This dynamics results to take into account the main dynamic features of polymer molecules.

We have performed numerical simulations of the model on the cubic lattice of different lattice sizes ($L = 24, 32, 40$) 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 with probability $p$, which coincides with the monomer concentration on the main lattice in the thermodynamic limit \cite{18}. 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.

First, a qualitative phase diagram has been determined, studying the onset of the gel phase varying $p$ and $p_b$: on this basis we have then fixed $p_b = 1$ and let $p$ vary in the interesting range from the sol to the gel phase. The percolation transition has thus been studied via the percolation probability $P$ and the mean cluster size $\chi$ on lattices of different size. From their finite size scaling behaviours we have obtained the percolation threshold $p_c \simeq 0.718 \pm 0.005$, the critical exponents $\nu \simeq 0.89 \pm 0.01$ for the percolation correlation length $\xi$ and $\gamma \simeq 1.8 \pm 0.05$ for the mean cluster size $\chi$ (fig.\ref{fig:1}). These results do agree with the random percolation
critical exponents [12].

The system evolves according to the bond fluctuation dynamics, i.e. the monomers diffuse with random local movements along lattice directions within the excluded volume constraint and produce the bond length fluctuation among the allowed values. In fact the BF dynamics can be easily expressed in terms of a lattice algorithm and on a cubic lattice it can be shown that the bond lengths which guarantee the SAW condition are $l = 2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10}$ in lattice spacing units [17]. In fig.(2) a simple example of time evolution of a cluster is shown.

We remind that the percolation properties are not modified during the dynamic evolution of the system, as it is not possible to break or form bonds, which would change the cluster size distribution.

In order to determine the viscosity critical behaviour we use two independent ways, based respectively on the diffusion behaviour of the clusters and on the relaxation times. Within the study of diffusion properties in the system an interesting picture is obtained with a simple scaling argument on the diffusion coefficients as presented in [19]: the sol at the sol-gel transition is a heterogeneous medium formed by the solvent and all the other clusters

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1 The same agreement with the random percolation critical exponents has already been obtained in the $d = 2$ version of the model [18]. Here it is worth to mention that this case on a cubic lattice with monomer functionality $f = 4$ is rather the problem of a restricted valence percolation. This is a percolation on a lattice where the number of bonds emanating from the same site is restricted or no site may have more than a fixed number of $nn$. It does reproduce the occurrence of valence saturation for monomers in the gelation process. If the number of allowed bonds per site is greater than 2 this problem is expected to belong to the same universality class as the random percolation [11]. As the restriction on the number of bonds per monomer clearly introduces a correlation effect in the process of bond formation we have optimized our algorithm to minimize this effect and actually obtained a good agreement with the random percolation exponents.
of different sizes, with the mean cluster size rapidly growing near the percolation threshold. A cluster with gyration radius $R$ can be seen as a probe diffusing in such a medium: as long as its radius is much greater than the value of the percolation correlation length in the sol the Stokes-Einstein relation is expected to be valid, and the diffusion coefficient $D(R)$ of the probe will decrease proportionally to the inverse of the viscosity coefficient of the medium, $D(R) \sim 1/R^{d-2} \eta$. Then 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 $D(R) \sim 1/R^{d-2} \eta(R)$ should be expected to hold.

As the percolation threshold is approached the probe diffuses in a medium where a spanning cluster appears with a self-similar structure of holes at any length scale. At the percolation threshold the viscosity coefficient of the sol (the bulk viscosity coefficient) diverges as $\eta \sim (p_c - p)^{-k}$ and for the viscosity coefficient depending on $R$ the scaling behaviour $\eta(R) \sim R^{k/\nu}$ should be expected. When $R$ is of the order of the correlation length then $\eta(R) \sim \eta$. Following this scaling argument $D(R) \sim 1/R^{d-2+k/\nu}$ at $p = p_c$.

Within this description the use of the Rouse model would consist in taking $D(s) \sim 1/s$ for a cluster of size $s$. Then for large enough cluster sizes $s$ in percolation $s \sim R^{d_f}$ where $d_f$ is the fractal dimensionality of the percolating cluster. Taking $D(R) \sim 1/R^{d_f}$ leads to $k \sim (d_f + 2 - d)\nu$, which again gives $k = 2\nu - \beta$, the Rouse exponent given in [14].

We then study the diffusion of monomers and clusters via the mean square displacement of the center of mass. For a cluster of size $s$ (an $s$-cluster) this quantity is calculated from the coordinates of its center of mass $\vec{R}_s(t)$ as

$$\langle \Delta R^{2}_s(t) \rangle = \frac{1}{N_s} \sum_{\alpha=1}^{N_s} (\vec{R}^{s\alpha}_s(t) - \vec{R}^{s\alpha}_s(0))^2$$

(1)

where the index alpha refers to the $\alpha$th $s$-cluster and $N_s$ is the number of $s$-clusters so that this quantity is averaged over all the $s$-clusters. All the data refer to a lattice size $L = 32$ and the calculated quantities have been averaged over $\sim 30$ different site and bond configurations of the same $(p, p_b)$ values [18].

On the basis of the theory of Brownian motion and a simple Rouse model approach [13] the
center of mass of a polymeric molecule is expected to behave as a Brownian particle after a sufficiently long time. Indeed we find a linear dependence on time in the long time behaviour of \( \langle \Delta R_s^2(t) \rangle \) and determine the diffusion coefficient of an \( s \)-cluster in the environment formed by the solvent and the other clusters. In fig.(3) it is shown how the asymptotic diffusive behaviour is reached after a time which increases with the cluster size \( s \), due to the more complicated relaxation mechanism linked to the inner degrees of freedom in the molecule. As \( p \) increases towards \( p_c \) the \( s \)-clusters move in a medium which is more viscous and whose structure is more and more complex. As a consequence, we observe an immediate increase in the time necessary to reach the asymptotic diffusive behaviour of the center of mass motion for all the cluster sizes.

At \( p = p_c \) we have calculated the diffusion coefficients of clusters of size \( s \) and radius of gyration \( R \) in order to obtain the dependence \( D(R) \). The diffusion coefficients decrease with the increasing size of the cluster, as it is expected, but after a gradual decrease their values dramatically go to zero. This behaviour which is due to the block of the diffusion for finite cluster size in a finite system has allowed to consider only cluster size up to \( s = 30 \). In fig.(4) we have plotted \( D(R) \) for different cluster sizes \( (s = 5 \text{ to } 30) \): the data results to be well fitted by a power law behaviour. Using this scaling argument which gives the prediction \( D(R) \sim 1/R^{1+k/\nu} \) we obtain for the viscosity coefficient a critical exponent \( k \sim 1.3 \pm 0.1 \).

We here briefly mention that on the other side the diffusion coefficients of very small clusters are not expected to be linked to the macroscopic viscosity, and in fact the diffusion coefficient of monomers does not go to zero at \( p_c \), but has a definitively non-zero value for \( p > p_c \) (fig.(5)). It is also interesting to notice that the data seems to agree with a dependence \( e^{-1/1-p} \), suggesting some cooperative mechanism in the diffusion process.

In order to study the viscosity in the system independently from the scaling hypothesis given before, we have studied the relaxation times via the density time autocorrelation functions. We have calculated the time autocorrelation function \( g(t) \) of the number of pairs of \( nn \)
monomers $\varepsilon(t)$, defined as

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

where the bar indicates the average over $t'$ (of the order of $10^3$ time intervals) and the brackets indicate the average over about 30 different initial site and bond configurations.

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. This is a sign of the existence of a distribution of relaxation times which cannot be related to a single time and this behaviour had already been observed in the $d = 2$ study of the model. It is a typical feature of polymeric systems where the relaxation process always involves the rearrangement of the system over many different length scales \[21,23\]. This idea of a complex relaxation behaviour is further confirmed by the good fit of the long-time decay of the $g(t)$ with a stretched exponential law (fig.(6)). 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 critical regime \[24,25\]. The picture we obtain via the density time autocorrelation functions is coherent and very close to the experimental characterization of the sol at the gelation threshold.

For $p \sim p_c$ we have then fitted the $g(t)$ with a stretched exponential behaviour $e^{(-t/\tau_0)^\beta}$ (fig.(7)), where $\beta \sim 0.3$. This value is quite lower than the ones experimentally obtained in ref. \[24\] for a gelling solution or analytically predicted in ref. \[26\] for randomly branched polymers: this discrepancy could be due to the fact that our data refer to a quite narrow region near the gelation threshold where $\beta$ is expected to assume the lowest value. On the other hand this value of $\beta$ agrees with the experimental results in ref. \[25\] and with the asymptotic value of the stretched exponential exponent $\beta$ in both Ising spin glasses and polymer melts close to the freezing point in ref. \[27\].

The characteristic time $\tau_0$ varies with $p$ and increases as $p_c$ is approached. Plotting $\tau_0$ as a function of $(p_c - p)$ the data can be fitted by a power law dependence, with a critical
exponent $\sim 1.27 \pm 0.05$ (fig.8), very close to the viscosity critical exponent obtained from the diffusion properties. This characteristic time extracted from the long time relaxation behaviour diverges at the percolation threshold because of the passage between two different viscoelastic regimes.

The most immediate way to characterize the distribution of the relaxation times in the system is the average characteristic time defined as

$$\tau(p) = \frac{\int_0^t t' g(t')dt'}{\int_0^t g(t')dt'}$$

which is a typical macroscopic relaxation time and can be directly linked to the viscosity coefficient.

Numerically in the eq.(3) $t$ has been chosen by the condition $g(t') \leq 0.001$ for $t' \geq t$. This characteristic time grows with $p$ and diverges at the percolation threshold according to the critical behaviour

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

with an exponent $k \simeq 1.3 \pm 0.03$ (fig.8), which gives the critical exponent for the viscosity at the sol-gel transition. From an immediate comparison between $k$ and the critical exponent for $\tau_o$ there seems to be a unique power law characterizing the divergence of the relaxation times in the system approaching from below the transition threshold.

For a more detailed description of the distribution of relaxation times at the sol-gel transition together with a study of the frequency dependence of the viscoelastic properties see references [8,22,24].

The critical exponent obtained for the viscosity critical behaviour is then $k \sim 1.3$ and it well agrees with the value of $k$ previously given, although independently obtained. This value is quite close to the one experimentally measured in silica gels [7,19] andInterestingly these systems are characterized by a polyfunctional condensation mechanism with tetrafunctional monomers, which is actually very similar to the case simulated here. This result is also close to the value obtained by recent accurate measurements in PDMS [8].

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It does not agree with the *random superconducting network* exponent $k = 0.7$ \cite{13} according to the de Gennes’ analogy, whereas it is quite close to the Rouse exponent discussed above. We have already mentioned that a Rouse-like description of a polymer solution corresponds to a complete screening of the entanglement effects and the hydrodynamic interactions and is usually considered not realistic enough. Actually the entanglement effects could be not so important in the relaxation mechanism in the sol on the macroscopic relaxation time scale: due to the fractal structure of the gel phase the system is in fact quite fluid, probably there is no blocking entanglement yet and such temporary entanglements relaxe on a smaller time scale, not really affecting the macroscopic relaxation time \cite{28}. Furthermore the screening effect of the hydrodynamic interactions in a polymeric solution in the semidiluted regime can be quite strong, drastically reducing the range of the interactions so that the Rouse model results to be in fact very satisfactory \cite{13}. This could reasonably be the case of the sol at the gelation threshold too, and the deviation of the real critical exponent from the Rouse value would turn out to be actually very small.

The numerical simulations have been performed on the parallel Cray-t3e system of CINECA (Bologna, Italy), taking about 15000 hours of CPU time. The authors acknowledge partial support from the European TMR Network-Fractals c.n.FMRXCT980183 and from the MURST grant (PRIN 97). This work was also supported by the INFM Parallel Computing and by the European Social Fund.
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FIGURES

FIG. 1. Data collapse for lattice sizes $L = 24, 32, 40$ for the percolation probability $P$ (a) and for the mean cluster size $\chi$ (b): the best collapse is obtained with $p_c = 0.718 \pm 0.05$, $\nu = 0.89 \pm 0.01$, $\gamma = 1.8 \pm 0.05$.

FIG. 2. Four different possible configurations for a cluster formed by four monomers in the time evolution according to the bond fluctuation dynamics. We consider the subsequent monomer movements: in a the bond lengths are (starting from the upper center bond and clockwise) $l = \sqrt{5}, 3, 3, 2$; moving forward the upper left monomer we have b with $l = 2, 3, 3, \sqrt{5}$; from this configuration moving right the other left monomer we have c with $l = 2, 3, \sqrt{6}, \sqrt{6}$; then moving right the front monomer on the right leads to d and $l = 2, \sqrt{10}, \sqrt{6}, \sqrt{6}$.

FIG. 3. $\langle \Delta R_s^2(t) \rangle / t$ as a function of time for $p = 0.69$ for different cluster sizes; from top to bottom $s = 1, 2, 3, 4, 5, 8, 10$. The broken lines correspond to the asymptotic values, i.e. the values of the diffusion coefficients. The data have been averaged over 32 different configurations.

FIG. 4. The diffusion coefficient at $p_c$ averaged over 32 different configurations for different cluster size as a function of the cluster radius of gyration $R$: supposing the scaling behaviour $D(R) \sim 1/R^{1+k/\nu}$, gives $k \sim 1.3 \pm 0.02$.

FIG. 5. The monomer self-diffusion coefficient as function of $p$. The data show how the self-diffusion coefficient of monomers is not linked to the macroscopic viscosity diverging at the gel point. $D(s = 1)$ becomes numerically undistinguishable from zero only at $p > p_c$ and the data are well fitted with the dependence $\sim e^{-1/1-p}$ (the continuous line).

FIG. 6. Time autocorrelation function $g(t)$ of the density of $nn$ monomers defined in eq.(2) as function of time for various $p$. From top to bottom $p = 0.705, 0.7, 0.69, 0.66, 0.5$ (data averaged over $\sim 30$ different configurations).

FIG. 7. Stretched exponential behaviour $e^{-(t/\tau_0)^\beta}$ of the long time tail of the time autocorrelation function $g(t)$ for $p = 0.66$ (bottom) and $p = 0.69$ (top).
FIG. 8. The characteristic time $\tau_0$ obtained from the stretched exponential fit of the time autocorrelation function long time behaviour as a function of $(p_c - p)$. The data are well fitted by a power law with an exponent $1.29 \pm 0.03$.

FIG. 9. The characteristic integral time $\tau$ calculated according to eq.(1) as a function of $(p_c - p)$. The data are well fitted by a power law with a critical exponent $k \sim 1.31 \pm 0.05$. 
figure 2
\[ \langle \Delta R_s^2(t) \rangle / t \]
