Elastic critical behaviour in a 3d model for polymer gels

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Abstract

The elastic response in polymeric gels is studied by means of a percolation dynamic model. By numerical simulations the fluctuations in the gyration radius and in the center of mass motion of the percolating cluster are determined. Their scaling behaviour at the gelation threshold gives a critical exponent for the elastic modulus $f \sim 2.5 \pm 0.1$ in agreement with the prediction $f = d\nu$.

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I. INTRODUCTION

The elastic response in polymer gels is due to the presence of the polymeric network formed in the gelation process: this random structure makes the system able to respond to external stresses. Due to the large possibility of conformational changes which characterizes this macromolecular phase, there is an entropic term contributing to the elastic properties of the system. This picture is typical of gelling systems and may fit a wide range of very different materials. Then because of the different role played by the entropic term and the particular features of the polymeric networks, a rich phenomenology is produced.

The viscoelastic behaviour of gelling materials and the mechanisms at its origin certainly represent a central issue in soft matter physics and have a high relevance to a wide range of applications from food processing to materials science. On the other hand these materials show many typical features of complex systems and their study is connected to some fundamental problems in soft matter physics, from the entropic elastic behaviour, which we are interested in here, to glassy dynamics. As a consequence these systems are intensively investigated both experimentally and by means of statistical mechanics models, bringing up a lively debate.

In particular here we study the critical behaviour of the elastic response of the system as the gelation process takes place producing the polymeric network: in a gelling system the elastic modulus starts growing at the gelation threshold with a power law behaviour, usually expressed in terms of the polymerization degree. In the experiments performed on different gelling materials the value of the critical exponent $f$ describing the critical behaviour of the elastic modulus appears to be close to either $f \sim 2$, or $f \sim 3$, or else $f \sim 4$. The value $f \sim 2$ is actually observed in experiments on agarose gel [1], gelatin gels [2], some silica gels (TEOS) [3]. Within statistical mechanics models it corresponds to the prediction based on the de Gennes’ analogy between the elasticity of a percolating random network of Hookean springs and the conductivity in a random percolating network of resistors [4]. The critical exponent $f \sim 3$. has been observed in diisocianate/triol gel [7], in epoxy resins
It is very close to the value $f = d\nu$, where $d$ is the dimensionality of the system and $\nu$ is the critical exponent of the connectedness length $\xi$, predicted in ref. [11] which in $3d$ gives $f \sim 2.64$ (in mean field both $d\nu$ and the random resistor network exponent are equal to 3). Following the argument in ref. [11] this exponent would then correspond to the case of a dominating entropic term, evaluated by means of scaling arguments for the percolating network: the elastic energy of the system is due to the entropic elasticity of the macrolink whose length is of the order of the connectedness correlation length. Finally the value $f \sim 4$ can be linked to the prediction of the bond-bending model $f = d\nu + 1$ [12,13] or alternatively $f = t + 2\nu$ [14,15], which in $3d$ give $f \sim 3.7$. This would imply that within the elastic energy describing the system there is a bending term playing a relevant role in the elastic response of the network. This critical behaviour is typical of some colloidal gels [16]. The clustering of the experimental values for the elasticity critical exponent in gels around discrete values suggests the possibility of correspondently individuating different universality classes, which should be characterized by some intrinsic features of the networks formed in the materials.

Recent numerical studies via molecular dynamics [5] and Monte Carlo simulations [6] of percolating networks of tethered particles with no hard core interactions have shown that the shear modulus critical exponent is $\sim 1.3$ in $d = 2$ and $\sim 2.$ in $d = 3$. Monte Carlo simulations of two and three-dimensional percolating networks of tethered particles with hard core repulsion [6] find consistent results for the shear modulus critical exponent. These results agree with the de Gennes prediction and with some experimental results.

Within the numerical studies we have approached the study of this problem introducing a percolation dynamic model, and directly investigating the dynamic viscoelastic properties as the percolation transition takes place. Our model introduces in the percolation model the bond-fluctuation dynamics, which takes into account the conformational changes of the polymer molecules and the excluded volume interactions. This model has been translated in a lattice algorithm and studied via numerical simulations on hypercubic lattices. Actually it presents many fundamental features of the gelation phenomenology and has already allowed
to study the critical behaviour of the viscoelastic properties and the relaxation process in
gelling systems in the sol phase [19]. Numerical simulations of the model in $d = 2$ [20] have
shown that the elasticity critical exponent is $\sim 2.7$, a value which agrees with the prediction
$f = d\nu$ in [11]. The study of the model in $d = 3$ is of great interest to check the elasticity
critical behaviour and to eventually compare the findings with the experimental results. We
here present the results of large scale 3d simulations: the data show that $f \sim 2.5 \pm 0.1$,
again in agreement with the prediction $f = d\nu$, coherently with the findings in $d = 2$.

In the next section we present the model and the details of the numerical simulations, in sec-
tion III the elastic response of the percolating cluster is discussed and a scaling behaviour is
obtained; in section IV the results of the numerical simulations are presented and discussed;
section V contains concluding remarks.

II. MODEL AND NUMERICAL SIMULATIONS

We consider a solution of tetrafunctional monomers of concentration $p$. The monomers
interact via excluded volume interactions, i.e. a monomer occupies a lattice elementary
cell and two occupied cells cannot have common sites. Nearest neighbours or next-nearest
neighbours are instantaneously linked by a permanent bond with probability $p_b$. In terms
of these two parameters the percolation line can be determined via the critical behaviour of
the percolation properties, individuating the sol and the gel phase in the system. Actually
in the simulation we fix $p_b = 1$ and study the system varying $p$ [19–21]. The percolation
quantities critical exponents agree with the random percolation predictions [18] (e.g. $\gamma \simeq
1.8 \pm 0.05$ and $\nu \simeq 0.89 \pm 0.01$ in $3d$ [19]). The monomers free or linked in clusters diffuse
via random and local movements on the lattice according to the bond-fluctuation dynamics
[22], which is ruled by the possibility of varying the bond lengths within a set of values
determined by the excluded volume interactions and the SAW condition. This produces a
high number of different bond vectors and we consider the case of permanent bonds, which
corresponds to the strong gelation process. In $3d$ the allowed bond lengths on the cubic
lattice are \( l = 2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10} \) and in Fig.1 an example of different allowed configurations for a polymer molecule is shown.

We here present the results of extended numerical simulations of the model in the gel phase to study the elastic response in the system. It is worth noticing that there is no elastic potential energy for the bond vectors and then the elastic behaviour is purely entropic implying that our study is performed at finite temperature.

The data presented here refer to lattice sizes \( L \) ranging from 12 to 32, and have been averaged over 30 different realizations. The simulations have been performed on the CRAY – T3E system at CINECA taking more than 30000 hours/node of CPU time.

### III. ELASTIC RESPONSE IN THE GEL PHASE

We study the elastic response in the gel phase 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 \( L, K \sim EL^{d-2} \), 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 \( \sim \xi^{-\tilde{j}} \) (where \( \tilde{j} = f/\nu \)) one has

\[
K \sim L^{d-2} \xi^{-\tilde{j}} \tag{1}
\]

Following eq.(1) the macroscopic elastic constant presents the corresponding scaling behaviours as function of the system size \( L \) and of the distance from the percolation threshold \((p - p_c)\):
\[ p > p_c \quad K \sim L^{d-2} \]
\[ p = p_c \quad K \sim L^{-\tilde{z}} \]
\[ \text{fixed } L \quad K \sim (p - p_c)^f \]

where \( \tilde{z} = \tilde{f} - (d - 2) \).

An alternative way to obtain these scaling relations is to consider the percolating cluster as a network of nodes connected by macrolinks of linear size \( \xi \) [23]. Each macrolink can be considered as a spring with an effective elastic constant. At the percolation threshold there is only one macrolink spanning the system and its effective elastic constant coincides with the system macroscopic elastic constant \( K \).

In order to evaluate \( K \) we notice that for a spring of elastic constant \( K \) in a thermal bath at temperature \( T \), the mean fluctuation in the energy \( U \) is \( \langle \Delta U \rangle = \frac{1}{2} K \langle x^2 \rangle \), where \( x \) is the spring elongation. From the energy equipartition \( K \langle x^2 \rangle = k_B T \), so that at the equilibrium the elastic constant \( K \) is related to the the fluctuations in the spring length [24–27]. This result can be more generally obtained by means of the Fokker-Plank equation for the probability distribution of the spring elongation [24].

Therefore the macroscopic elastic constant of the gel phase is related to the fluctuations of the linear size of the infinite cluster, i.e. the squared fluctuations in the gyration radius of the percolating cluster \( \langle \Delta R_g^2 \rangle = \langle (R_g - \langle R_g \rangle)^2 \rangle, \quad K \sim 1/\langle \Delta R_g^2 \rangle \).

An alternative way to calculate the macroscopic elastic constant in the gel phase by means of the fluctuations in the unperturbed system is to consider the center of mass of the percolating cluster as a brownian particle, subject to a restoring force responsible for the elastic behaviour of the system. The restoring force introduces a limitation on the diffusive process of a brownian particle. Using the same argument based on the energy equipartition, the asymptotic equilibrium value \( \Delta \) of its displacement fluctuations \( \langle \Delta R^2(t) \rangle \) is inversely proportional to the elastic constant, i.e. \( \Delta \sim 1/K \).
IV. RESULTS

In order to numerically study the elastic response we have used both the approaches mentioned before namely we have calculated the average fluctuation of the gyration radius of the percolating cluster \( \langle \Delta R^2_g \rangle \) and the asymptotic value \( \Delta \) of the mean square displacement of its center of mass \( \langle \Delta R^2(t) \rangle \) [28].

In the first approach the average fluctuation in the gyration radius \( \langle \Delta R^2_g \rangle \) of the percolating cluster has been computed at the percolation threshold in system of different size \( L \) with periodic boundary conditions. In Fig.2 \( \langle \Delta R^2_g \rangle \) at \( p_c \) is shown in a log-log plot as function of the lattice size \( L \). In the considered range the data are well fitted by a power law behaviour according to eq.(2), giving a critical exponent \( \tilde{z} \sim 1.9 \pm 0.1 \), i.e. \( z \sim 1.7 \pm 0.1 \). As \( \tilde{z} = \tilde{f} - (d - 2) \), \( f = z + (d - 2)\nu \) and this result gives \( f \sim 2.6 \pm 0.1 \).

In the second approach we have calculated \( \langle \Delta R^2(t) \rangle \) at different steps of the gelation process, i.e. as \( p \) grows above the percolation threshold \( p_c \sim 0.718 \pm 0.005 \) [19], and at \( p_c \) for different lattice sizes. In these simulations hard-wall boundary conditions have been used [29]. In the gel at the gelation transition the percolating cluster is a quite loose network, the center of mass is rather free and the elastic response is weak. As the gelation process goes on, the network tightens becoming more rigid, the elastic constant of the system increases and the center of mass motion is progressively constrained. This would be then the physical mechanism producing the critical behaviour of the elastic response for a critical gel. In agreement with our picture \( \langle \Delta R^2(t) \rangle \) grows with time up to a limiting plateau value \( \Delta \) as it is shown in Fig.3. This quantity is inversely proportional to the elastic constant of the system \( \Delta \sim 1/K \) and increases as the percolation threshold is approached from above.

In Figures 4,5 and 6 the scaling behaviour obtained for \( \Delta \) is presented.

In Fig.4 \( \Delta(L,p) \) for \( p >> p_c \) (\( p = 0.85 \)) is shown in a double logarithmic plot: being far from the percolation threshold the system is reasonably homogeneous and in fact the scaling behaviour as \( \Delta \sim L^{-0.99\pm0.1} \) is observed, in agreement with the behaviour \( K \sim L^{d-2} \).

In Fig.5 \( \Delta(L,p = p_c) \) is shown in a double logarithmich plot as a function of the lattice size \( L \):
the data exhibit a behaviour \( \Delta \sim L^{\tilde{z}} \) with \( \tilde{z} \sim 2.0 \pm 0.1 \). This result again gives \( f \sim 2.6 \pm 0.1 \).

Finally in Fig.6 \( \Delta(p - p_c) \) is plotted for the lattice size \( L = 32 \): we fit the data with a power law behaviour (eq.(2)) and obtain a critical exponent \( f \sim 2.5 \pm 0.1 \).

It is straightforward to notice that all these numerical results can be coherently interpreted in terms of the scaling relations obtained for \( K \).

The value of the critical exponent \( f \sim 2.6 \) is in good agreement with the prediction \( f = d\nu \) of ref. [11], therefore supporting the picture there proposed, and consistent with the value obtained in the 2d study of the model [20].

Due to the limited extension of the critical parameter \( (p - p_c) \) and of \( L \) here investigated the eventual occurrence of a crossover to a different exponent cannot be excluded.

V. CONCLUSIONS

The numerical results of Figures 2,5 and 6 show that \( \tilde{z} = 2.0 \), coherently agreeing with the prediction \( f = d\nu \). On the whole they support the scaling picture we propose and the argument of ref. [11]. They also agree with some experimental results [7]-[10]. This result has been obtained via two independent calculations giving consistent numerical values and is also consistent with the value previously obtained in the 2d study.

On the other hand the recent numerical works on entropic elastic models of refs. [5,6] find a good agreement with the de Gennes prediction. These results, together with the experimental data, seem to suggest the possibility that there are two distinct universality classes characterized one by an exponent \( f = d\nu \) and another by the electrical analogy exponent \( f = t \), which in 3d are respectively \( \sim 2.64 \) and \( \sim 2.0 \). However since the models in the different numerical studies are rather similar the possibility of a crossover between different dynamic regimes, as it is observed in some experiments [3], cannot be completely excluded.

In both cases these results give a hint for the interpretation of the experimental data and indicate the aspects which should be further investigated.

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Above the percolation threshold the percolating cluster can be considered as a network
made of nodes connected by macrolinks of linear dimension $\xi$. Each macrolink can be
considered as a spring of elastic constant $k$. For a system of size $L$ it can be regarded
as $L/\xi$ elements in series, each element being made of $(L/\xi)^{d-1}$ springs in parallel.
The macroscopic elastic constant is then $K = k(L/\xi)^{d-1}(L/\xi)^{-1}$. Let $z$ be the critical
exponent for the elastic constant $k$ of the links of length $\xi$ decreasing to zero at the
percolation threshold with a power law behaviour $k \sim (p - p_c)^z$ [11,13,18]. Then we
obtain a scaling behaviour for the macroscopic elastic constant $K \sim (L/\xi)^{d-2}\xi^{-\tilde{z}}$, where
$\tilde{z} = z/\nu$. This means that $K \sim \xi^{-\tilde{z}-(d-2)}L^{d-2}$ and therefore again $K \sim L^{d-2}(p -
p_c)^{z+(d-2)\nu}$.
In both approaches we stress that the fluctuations for the percolating clusters have been calculated in presence of the finite clusters and the other free monomers dynamically evolving according to the same fluctuation dynamics, namely we have studied the dynamic evolution of the percolating cluster embedded in the medium formed by the finite clusters, free monomers and solvent.

With the hard-wall boundary conditions, or free boundary conditions, the fluctuation of the center-of-mass motion of the percolating cluster, whose size is $\sim L$, corresponds to the macroscopic elastic response of the system. With these boundary conditions the simulation is actually performed at constant volume, i.e. there is a force acting on the percolating cluster which confines it inside the volume $L^3$. Following the picture presented at the end of section III, let us consider the very simple case of a spring of elastic constant $K$ in a thermal bath at temperature $T$. In order to take into account the effect of the boundary conditions on the system we are studying, let us consider a constant force of module $f$ acting on it along the direction $\hat{x}$ of its elastic deformation and introducing in the energy a linear term in the deformation $x$. The mean energy of the system is now $\langle U \rangle = \frac{1}{2}K\langle x^2 \rangle - \langle fx \rangle$. If we assume that $\langle fx \rangle \sim f\langle x \rangle$ the mean fluctuation of the energy is again given by $\langle \Delta U \rangle = \frac{1}{2}K\langle (x-\langle x \rangle)^2 \rangle$, with $\langle x \rangle = f/K$. On the other hand $\langle x \frac{\partial U}{\partial x} \rangle = K_B T = K\langle x^2 \rangle - f\langle x \rangle$ and with the assumption $\langle fx \rangle \sim f\langle x \rangle$ gives $K\langle (x^2 - \langle x \rangle)^2 \rangle = K_B T$. Then again $\langle \Delta x^2 \rangle = \langle (x^2 - \langle x \rangle)^2 \rangle \sim 1/K$. 

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FIGURES

FIG. 1. An example of time evolution of a cluster formed by four monomers according to the bond-fluctuation 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 right the other left monomer in b one has c with \( l = 2, 3, \sqrt{6}, \sqrt{6} \); moving right the front monomer in c the d configuration is obtained with \( l = 2, \sqrt{10}, \sqrt{6}, \sqrt{6} \).

FIG. 2. 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 \( \tilde{\nu} \sim 1.9 \pm 0.1 \) is obtained. Here and in the following figures the lengths are expressed in units of lattice spacing.

FIG. 3. The mean square displacement of the center of mass of the percolating cluster \( \langle \Delta R^2(t) \rangle \) as function of time for different value of the monomer concentration \( p \): from below \( p = 0.8, 0.77, 0.76, 0.75 \). The dashed lines correspond to the asymptotic plateau values \( \Delta \) which grows approaching \( p_c \). The data refer to a lattice size \( L = 32 \). The unit time here is the MonteCarlo step per particle.

FIG. 4. Log-log plot of \( \Delta(L,p) \) for \( p >> p_c \) (the data refer to \( p = 0.85 \)) as function of \( L \): the data show a scaling behaviour \( \sim 1/L^{0.99\pm0.1} \).

FIG. 5. Log-log plot of the plateau values \( \Delta(L, p = p_c = 0.718) \) as function of \( L \): the data are fitted by a power law giving the critical exponent \( \tilde{\nu} \sim 2.0 \pm 0.1 \).

FIG. 6. The plateau values \( \Delta(L = 32, (p - p_c)) \) in a double logarithmic plot as function of \( (p - p_c) \): the best fit of the data close to the percolation threshold gives the critical exponent \( f \sim 2.5 \pm 0.1 \).
$\langle \Delta R^2(t) \rangle$
$\Delta(L, p=0.85)$

Figure 4
$\Delta(L, p=p_c)$

Figure 5
\[ \Delta(L=32, p-p_c) \]