

A percolation dynamic approach to the sol-gel transition

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys. A: Math. Gen. 31 1901

(<http://iopscience.iop.org/0305-4470/31/8/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.104

The article was downloaded on 02/06/2010 at 07:23

Please note that [terms and conditions apply](#).

A percolation dynamic approach to the sol–gel transition

Emanuela Del Gado[†], Lucilla de Arcangelis^{‡§} and Antonio Coniglio[†]

[†] Dipartimento di Scienze Fisiche, Università di Napoli ‘Federico II’, INFN Sezione di Napoli, Mostra d’Oltremare pad. 19, 80125 Napoli, Italy

[‡] Dipartimento di Fisica, Università de L’Aquila, INFN Sezione de L’Aquila, 67010 Coppito, L’Aquila, Italy

Received 7 July 1997

Abstract. The sol–gel transition is studied introducing the bond fluctuation dynamics within the percolation model in order to investigate both static and dynamic properties. Computer simulations on a square lattice have shown that the static properties agree with the random percolation model and the self-diffusion coefficients vanish at the percolation threshold. From the self-diffusion coefficients the critical behaviour of the viscosity at the sol–gel transition is determined, giving an exponent $s = 1.9 \pm 0.1$.

1. Introduction

The sol–gel transition is observed in a polymeric solution, the sol, where bond formation between different molecules is induced; it is characterized by a diverging viscosity and the appearance of an elastic behaviour. These properties are linked to the constitution inside the sol of a macroscopic polymeric structure, the gel phase [1, 2]. The viscoelastic behaviour at the sol–gel transition is expressed in terms of power laws for the viscosity η and the elastic modulus E [3–5, 7]. Experimental values for the critical exponents are very scattered: experimental determination for the viscosity critical exponent s has given values ranging from 0.6 to 1.6 and for the elastic modulus critical exponent t values from 1.8 to 3.9 in three dimensions [6, 7].

Because of the crucial role of connectivity, the percolation model has been successfully used to describe the transition [8, 9] and has given critical exponents for the mean weight averaged molecular weight, the mass distribution, the molecules gyration radius, and the gel fraction [10] which agree with the experimental measurements [14]. Kinetics of aggregation and dependence on the solvent have also been numerically studied [11–13].

The percolation model, however, gives a purely static description with no prediction on the viscosity and the elasticity critical behaviours [15]. On the other hand, experimental results do not allow a simple interpretation for both these quantities, leaving the critical behaviour of viscosity and elasticity as still an open problem.

In this paper we study the sol–gel transition within a percolation description, introducing the dynamics via the bond fluctuation model [16]. Since this model can be simply expressed in a lattice algorithm which allows the use of Monte Carlo techniques, we have carried out this study via computer simulations on a square lattice.

[§] Present address: Dipartimento di Ingegneria dell’Informazione, Seconda Università di Napoli, via Roma 29, 81031 Aversa (Caserta), Italy.

We consider the sol–gel transition in the case of strong gelation (e.g. polyfunctional condensation induced by light irradiation [23, 9]), where bonds are permanent and the transition exhibits a sharp threshold.

The paper is organized as follows. In section 2 we briefly describe the percolation dynamic approach based on the bond fluctuation model; in section 3 we present the numerical simulation; in sections 4 and 5 the results for the percolation properties and the diffusive behaviour are respectively discussed; conclusions follow in section 6.

2. The percolation dynamic approach

In a problem of strong gelation the process starts in a monomeric sol where permanent bonds are formed. We consider monomers to interact only via excluded volume interactions and bonds to form instantaneously, without modifying the monomer positions. The main parameters are then the monomer concentration and the bond density and the static properties can be described by random percolation [9].

Introducing an appropriate dynamics for monomers and clusters, dynamic properties can also be studied. It is then possible to determine the diffusion properties and calculate the diffusion coefficients D , which are linked to the viscosity η according to the Einstein's relation $D \propto 1/\eta$, near the percolation threshold.

We let the system evolve according to the bond fluctuation model. This is a coarse-grained model which has been introduced originally to study the dynamics of polymer chains [16–18]. In this model each fundamental monomeric unit in a molecule can move randomly, according to the excluded volume interaction constraint. Due to these random movements the bond lengths between monomers in the same molecule can fluctuate in a certain set of allowed values, which is determined by the self-avoiding walk condition. This model is found to reproduce the Rouse dynamics, as required [16, 17].

In the hypercubic lattice version each monomer occupies 2^d sites in d -dimensions, i.e. a lattice unit cell, and because of excluded volume interactions occupied cells cannot have common sites. Monomer movements are ruled by excluded volume and allowed bond lengths constraints.

3. The numerical simulation

In the numerical simulations we have considered a square lattice of size $L = 100$; each monomer occupies simultaneously four sites, which are vertices of a lattice elementary plaquette and two nearest neighbours (nn) monomers are always separated by an empty plaquette, i.e. two occupied plaquettes cannot have common sites[†]. We consider then the plaquette lattice with double lattice spacing and occupy its sites with probability p_m . In the thermodynamic limit this p_m coincides with the monomer concentration on the main lattice, i.e. the ratio between the present number of monomers and the maximum allowed number of monomers, which for example on a lattice $L = 100$ is 2500.

We let monomers distribute uniformly on the main lattice via a diffusion process lasting a fixed time interval (2000 Monte Carlo steps (MCS) per particle). Bonds are at this point instantaneously created with probability p_b between two nn monomers, or next nearest

[†] This model of single monomers is different from the hard square lattice gas model introduced in [19, 20], where two plaquettes may have common sites: it is possible to see that the formation of blocked structures, which dramatically slows down the diffusion process in the hard square lattice gas [21, 22], is not allowed in our case. In fact we verified that the monomer diffusion process has no such slowing down and is arrested only when the maximum monomer density is reached.

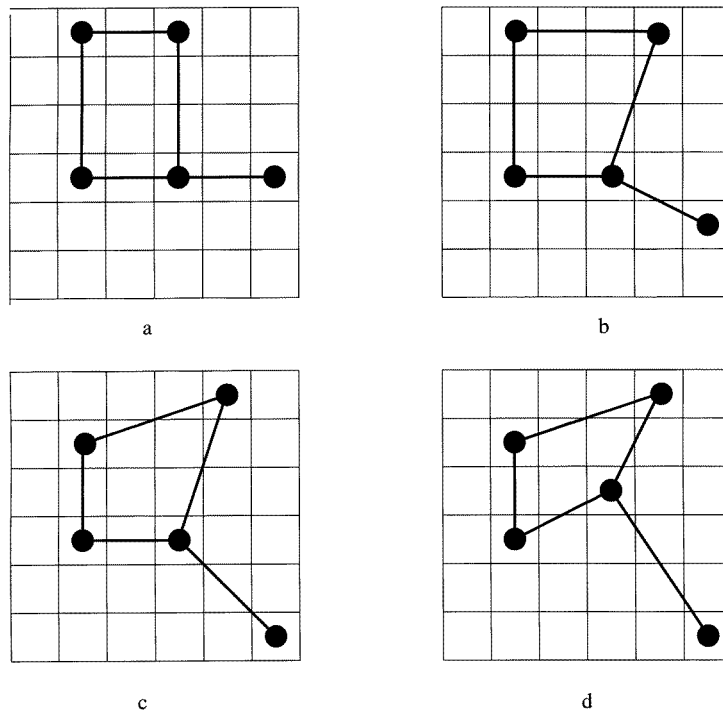


Figure 1. Possible configurations for a polymer consisting of five monomers: (a) a starting configuration when bonds of length $l = 2$ or $l = 3$ are present along lattice directions; (b)–(d) because of monomer displacements this configuration changes and bond lengths may assume every allowed value.

neighbours (nnn) along lattice directions (figure 1(a)). Since two monomers cannot be simultaneously nn and nnn, each monomer can be bonded to at most four other monomers ($d = 2$).

For each value of the pair (p_m, p_b) we determine the cluster size distribution using the Hoschen–Kopelman algorithm [25]. We calculate the mean cluster size and evaluate the percolation probability R corresponding to a (p_m, p_b) pair as the average number of configurations with a spanning cluster. The (p_m, p_b) pairs which correspond to a percolation probability $R = 0.5$ can be used to evaluate the curve of the gel onset. We have then fixed $p_b = 0.95$ and studied the system for different p_m values (which from now on we call simply p) in the sol phase, at the transition threshold and in the gel phase.

Monomers, free or linked in clusters, diffuse with one lattice spacing displacement along a direction randomly selected out of the four lattice directions. A monomer can move to one of the four nn plaquettes which have two sites in common with the one occupied at the moment. The other two sites of the new plaquette are required to be free, to prevent us from having two occupied plaquettes with common sites after the displacement.

Let us define the bond length as the Euclidian distance between two bonded monomers. In the diffusion process, because of the monomer displacements, the bond lengths are modified. We fix the maximum allowed bond length $l_{\max} = \sqrt{13}$ in order to avoid bond cuts and the minimum allowed bond length $l_{\min} = 2$ because of the excluded volume constraint [16]. The allowed values for the bond length l are then $l = 2, \sqrt{5}, 3, \sqrt{8}, \sqrt{10}, \sqrt{13}$ (figure 1). A single step in this diffusion process corresponds to an attempt to move each

single monomer on the lattice. After t time steps we calculate the coordinates of the centre of mass of a cluster of size s

$$\mathbf{R}_s(t) = \frac{1}{s} \sum_{i=1}^s \mathbf{r}_i(t) \quad (1)$$

and its mean-square displacement averaged over all s -clusters

$$\Delta R_s^2(t) = \frac{1}{N_s} \sum_{\alpha=1}^{N_s} (R_s^\alpha(t) - R_s^\alpha(0))^2 \quad (2)$$

where the index α refers to the α th s -cluster and N_s is the number of s -clusters.

We also calculate the number of nn monomer pairs $\varepsilon(t)$ and its time autocorrelation function $g(t)$ defined as

$$g(t) = \left\langle \frac{\overline{\varepsilon(t')\varepsilon(t'+t)} - \overline{\varepsilon(t')^2}}{\overline{\varepsilon(t')^2} - \overline{\varepsilon(t')^2}} \right\rangle \quad (3)$$

where the bar indicates the average over t' and the brackets indicate the average over the different initial site and bond configurations.

We have first used free boundary conditions, easily implemented in the algorithm, and obtained good data for the static properties and the qualitative behaviour of the autocorrelation functions. In the dynamic study free boundary conditions did not allow the particles to reach the diffusive regime close to the percolation threshold. We have then used periodic boundary conditions. Further studies of the autocorrelation functions with periodic boundary conditions are currently in progress.

4. Percolation properties

At $t = 0$, when the bonds have been created, after cluster counting we determine the percolation properties. As bonds are permanent, the cluster size distribution does not change with time. If s is the cluster size and n_s is the number of s -clusters per site, we calculate the mean cluster size as

$$\chi = \sum_s s^2 n_s \quad (4)$$

averaged over different initial site and bond configurations and evaluate the percolation probability R as explained in section 3.

To study these percolation quantities and their critical behaviour we have used finite-size scaling analysis and data collapse [25]. Therefore we have considered the percolation probability R and the mean cluster size χ to depend on L and p according to relations

$$R[(p - p_c), L] = F_1[(p - p_c)L^{\frac{1}{\nu}}] \quad (5)$$

and

$$\chi[(p - p_c), L] = L^{\frac{\gamma}{\nu}} F_2[(p - p_c)L^{\frac{1}{\nu}}]. \quad (6)$$

From Monte Carlo simulations on lattices with $L = 100, 120, 140$ at the fixed value $p_b = 0.95$ and varying p we have determined p_c and the exponent ν as the values which give the best data collapse for R ($p_c = 0.91 \pm 0.02$ and $\nu = 1.33 \pm 0.05$) (figure 2(a)). We have then used these values to study the χ data and we have determined the γ giving the best data collapse ($\gamma = 2.44 \pm 0.02$) (figure 2(b)). These values for γ and ν are in agreement with the random percolation exponents in two dimensions [25]. All the static properties are averaged over a number of configurations ranging from 120 to 700 depending on system size.

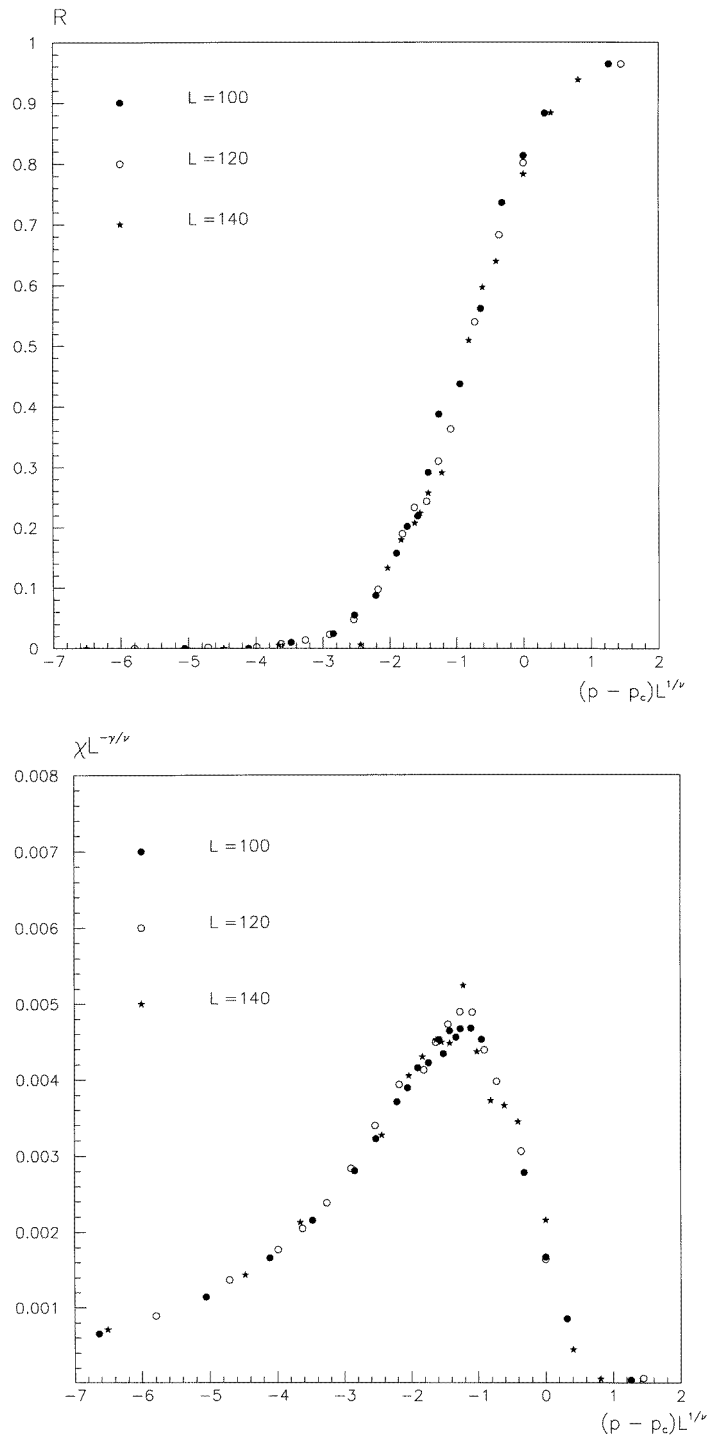


Figure 2. Data collapse for percolation probability R (a) for different cluster sizes ($L = 100, 120, 140$). The best collapse is obtained with $p_c = 0.91 \pm 0.02$ and $\nu = 1.33 \pm 0.05$. For the same lattice sizes, data collapse of the mean cluster size χ (b); the best collapse is obtained with $p_c = 0.91 \pm 0.02$, $\nu = 1.33 \pm 0.05$, $\gamma = 2.44 \pm 0.02$.

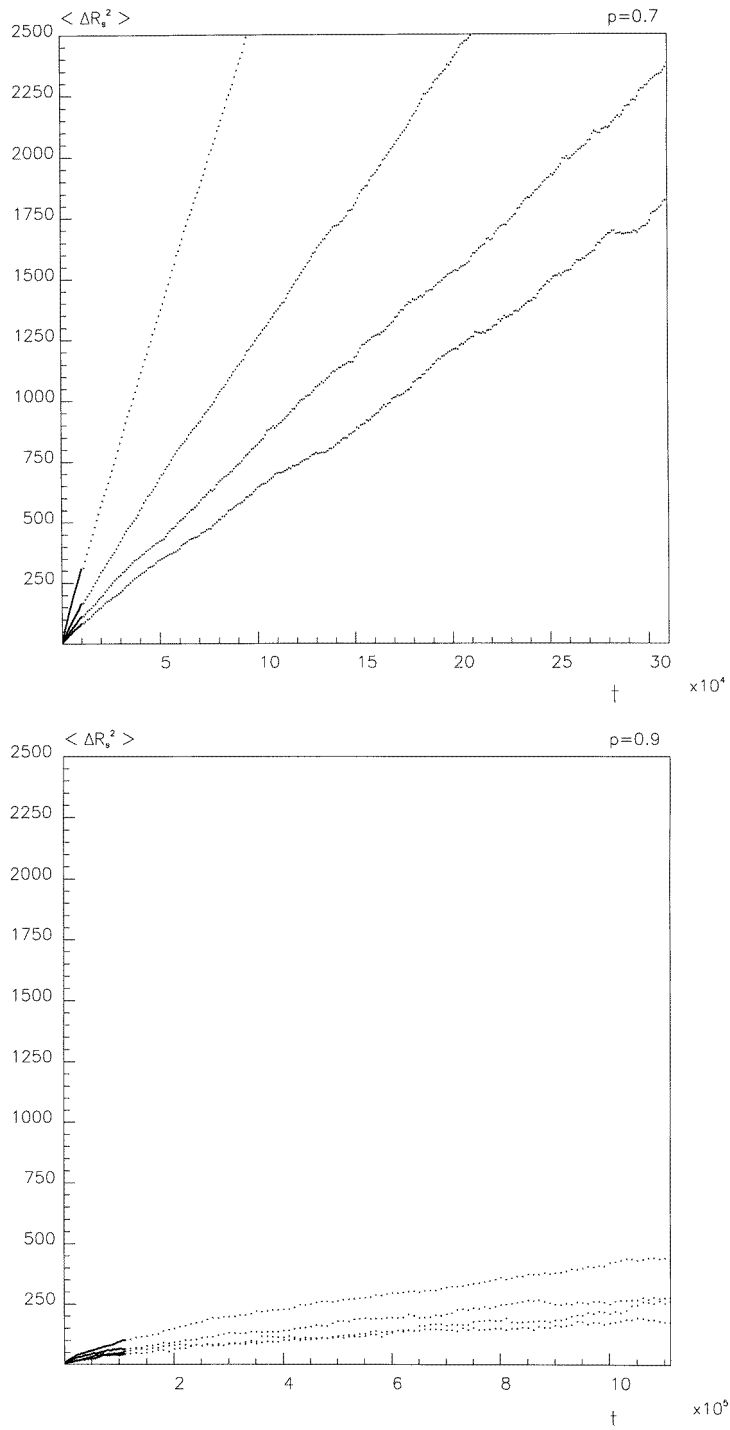


Figure 3. Mean-square displacement of the centre of mass as function of time for $p_b = 0.95$. The curves in each figure refer to cluster size $s = 1, 2, 3, 4$ (from top to bottom) and (a) 40 configurations at $p = 0.7$, (b) 10 configurations at $p = 0.9$.

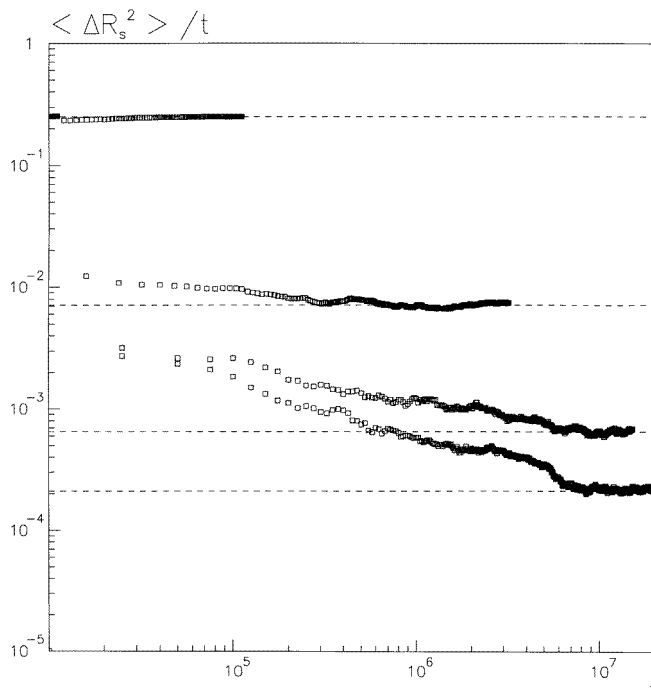


Figure 4. $\langle \Delta R_s^2(t) \rangle / 4t$ as function of time for $p_b = 0.95$ in a log-log plot for cluster size $s = 1$; from top to bottom $p = 0.4, 0.78, 0.86, 0.89$, and the broken lines correspond to the $\langle \Delta R_s^2(t) \rangle / 4t$ asymptotic value, i.e. the self-diffusion coefficients. The data are averaged over all s -clusters and a number of configurations ranging from 100 to 3 depending on p .

5. Diffusion properties

We have studied monomer diffusion on the lattice $L = 100$ with periodic boundary conditions. For each cluster size s , the centre of mass motion can be expressed, according to the theory of Brownian motion and the Rouse model [24], in terms of the self-diffusion coefficient D_s defined as

$$D_s = \lim_{t \rightarrow \infty} \frac{1}{4t} \langle \Delta R_s^2(t) \rangle \quad (7)$$

where the brackets as usual indicate the average over the different initial site and bond configurations.

The $\langle \Delta R_s^2(t) \rangle$ data for different cluster sizes as a function of p are shown in figure 3: we first observe for each value of p a decreasing self-diffusion coefficient with increasing cluster size. Big clusters are, in fact, supposed to move less easily in any monomer concentration condition.

If we now fix the cluster size and consider an increasing monomer concentration, we observe a decreasing self-diffusion coefficient as well for all cluster sizes. We could imagine a diffusing s -cluster as a molecule moving in the viscous fluid formed by the solvent and all the other molecules, therefore an increasing monomer concentration means an increasing intrinsic viscosity.

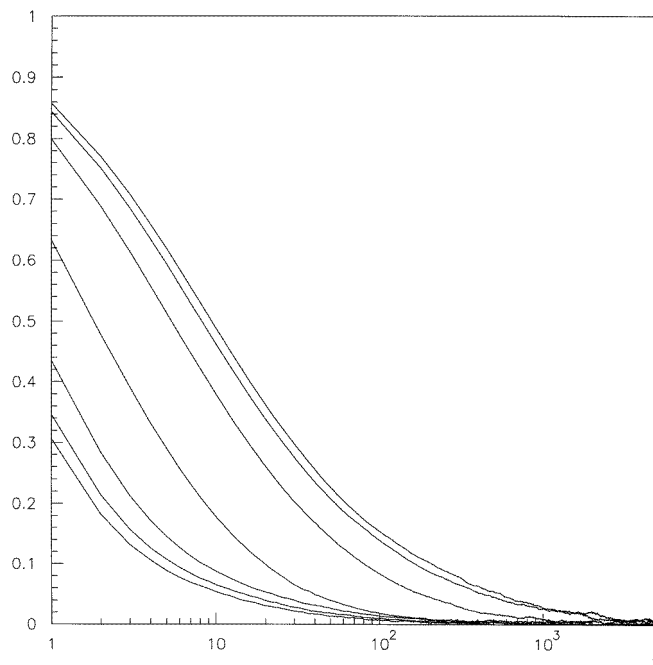


Figure 5. Time autocorrelation function $g(t)$ as function of time. The different curves refer to (from bottom to top) $p = 0.1, 0.4, 0.7, 0.8, 0.82, 0.85, 0.86$ and 10 configurations; for each curve $g(0) = 1$. The decay to zero becomes slower as p increases towards the percolation threshold $p_c = 0.91$.

In order to calculate D_s , we are interested in the long time diffusive behaviour, thus we have studied over several decades of time the quantity

$$\frac{1}{4t} \langle \Delta R_s^2(t) \rangle. \quad (8)$$

When this quantity attains a constant value we can say that the asymptotic diffusive regime has been reached and equation (8) provides the value of the self-diffusion coefficient D_s . The time needed to reach this diffusive behaviour increases with the monomer concentration p : in figure 4 we can see how for $p = 0.4$ and $p = 0.78$ the asymptotic regime is already reached at $t \simeq 10^5$ MCS whereas a much longer observation time is needed for $p = 0.86$ and $p = 0.89$.

The autocorrelation functions defined in equation (3) have been calculated for different p values and are shown in figure 5. In order to take the average over t' the entire observation time for each value of p is of the order of 10^6 MCS/ p . We observe that for p far enough from the percolation threshold the autocorrelation functions readily decay to zero, whereas their decay becomes slower as p increases up to the percolation threshold.

The self-diffusion coefficients D_s as function of p are presented in figure 6 for different cluster sizes s : for each cluster size D_s decreases and goes to zero at a value numerically indistinguishable from the percolation threshold.

We have focused on data for the $s = 1$ -clusters and calculated the critical behaviour for D_1 . Assuming the Einstein relation $D_1^{-1} \simeq \eta$ we can then determine the viscosity critical behaviour at the sol-gel transition. From the log-log plot (figure 7) we find that

$$\eta \propto (p - p_c)^{-s} \quad (9)$$

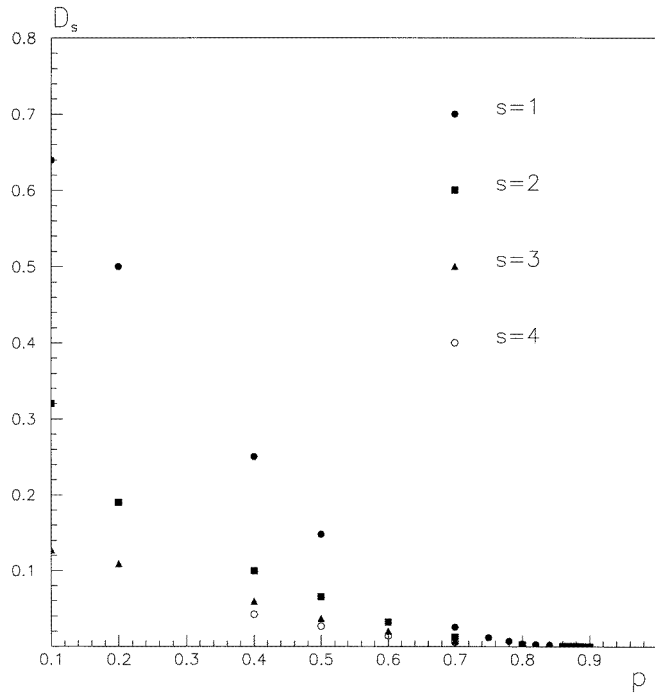


Figure 6. Self-diffusion coefficients D_s for $p_b = 0.95$ for different cluster sizes $s = 1, 2, 3, 4$ as function of p .

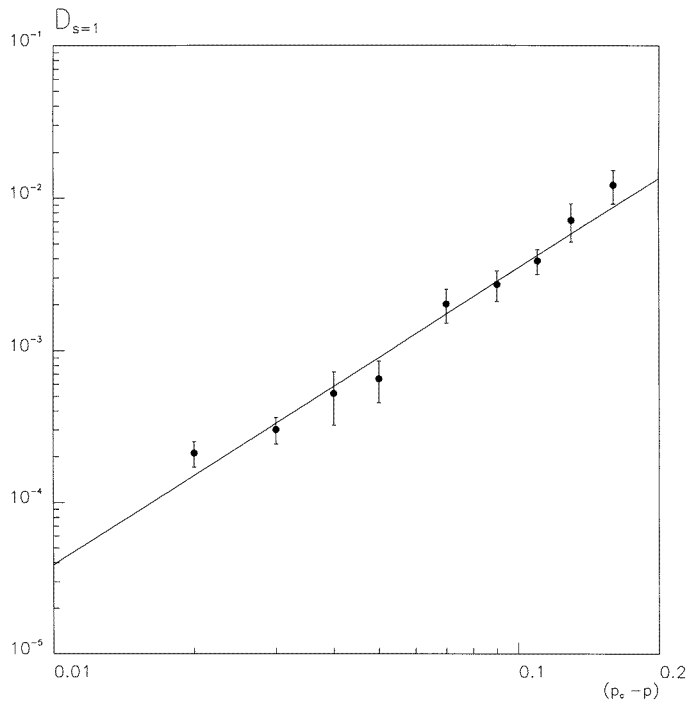


Figure 7. Log-log plot for self-diffusion coefficient D_1 critical behaviour for cluster size $s = 1$; the linear fit determines the critical exponent $s \simeq 1.9 \pm 0.1$.

with $s \simeq 1.9 \pm 0.1$. This evaluation of the viscosity critical exponent apparently does not agree with the exponent of conductivity in the random superconducting network $s \simeq 1.3$ [27], which is the value suggested by the de Gennes' analogy between this problem and gelation [26, 2].

6. Conclusions

We have studied the sol–gel transition introducing within the percolation model the bond fluctuation dynamics, which allows the description of bond conformational changes in polymers by means of fluctuating bond lengths. This model is aimed at studying the dynamic behaviour corresponding to the static transition. For strong gelation we have first identified the gelation transition and then studied the diffusion properties in the sol and calculated the self-diffusion coefficients. Our results show that the self-diffusion coefficients vanish at the percolation threshold with an exponent $s \simeq 1.9 \pm 0.1$. The behaviour of the autocorrelation functions indicates that the relaxation times become longer and longer as the percolation threshold is approached.

We are extending the study to the case $d = 3$ in order to allow the comparison with experimental data and to analyse the elasticity critical behaviour [15, 24].

References

- [1] Flory P J 1953 *Principles of Polymer Chemistry* (Ithaca, NY: Cornell University Press)
- [2] De Gennes P G 1980 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
- [3] Dumas J and Bacri J C 1980 *J. Physique Lett.* **41** L279
- [4] Gauthier-Manuel B and Guyon E 1980 *J. Physique Lett.* **41** L503
- [5] Adam M, Delsanti M, Okasha R and Hild G 1979 *J. Physique Lett.* **40** L539
- [6] Adam M, Delsanti M, Durand D, Hild G and Munch J P 1981 *Pure Appl. Chem.* **53** 1489
- [7] Lairez D, Adam M, Raspaud E, Emery J R and Durand D 1992 *Prog. Colloid. Polym. Sci.* **90** 37
- [8] Stauffer D 1981 *Physica* **106A** 177
- [9] Coniglio A, Klein W and Stanley H E 1982 *Phys. Rev. B* **25** 6805
- [10] Adam M, Coniglio A and Stauffer D 1982 *Adv. Polym. Sci.* **44** 103
- [11] Liu Y and Pandey R B 1996 *J. Chem. Phys.* **105** 825
- [12] Liu Y and Pandey R B 1996 *Phys. Rev. E* **54** 6609
- [13] Liu Y and Pandey R B 1997 *Phys. Rev. B* **55** 8257
- [14] Adam M 1991 *Makromol. Chem., Macromol. Symp.* **45** 1
- [15] Coniglio A and Daoud M 1981 *J. Phys. A: Math. Gen.* **14** L306
- [16] Carmesin I and Kremer K 1988 *Macromolecules* **21** 2819
- [17] Paul W, Binder K, Heermann D W and Kremer K 1991 *J. Physique* **1** 37
- [18] Carmesin I and Kremer K 1990 *J. Physique* **51** 950
- [19] Gaunt D S and Fisher M E 1966 *J. Chem. Phys.* **45** 2482
- [20] Ertel W, Froböse K and Jäckle J 1988 *J. Chem. Phys.* **88** 5027
- [21] Froböse K 1989 *J. Stat. Phys.* **55** 1285
- [22] Jäckle J, Froböse K and Knödler D 1991 *J. Stat. Phys.* **63** 249
- [23] Gordon M and Ross-Murphy S B 1975 *Pure Appl. Chem.* **43** 1
- [24] Doi M and Edwards S F 1986 *The Theory of Polymer Dynamics* (Oxford: Clarendon)
- [25] Aharony A and Stauffer D 1994 *Introduction to Percolation Theory* (London: Taylor and Francis)
- [26] de Gennes P J 1978 *C. R. Acad. Sci., Paris B* **131**
- [27] Coniglio A and Stanley H E 1984 *Phys. Rev. Lett.* **52** 1068