Viscoelastic Properties at the Sol-Gel Transition

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SUMMARY: We present a study of molecular dynamics at the sol-gel transition. Application of percolation and bond-fluctuation dynamics provides critical exponents for viscoelastic properties in a strong covalent gel and shows a complex non-exponential relaxation behaviour. The results are in good agreement with experimental findings and offer interesting pointers for discussions.

Introduction

The sol-gel transition is observed in a solution of branched polymer molecules when bond formation between different molecules is induced. It is phenomenologically characterized by the divergence of viscosity in the sol and by the appearance of an elastic behaviour in the gel phase. These phenomena correspond to the formation inside the sol of a macroscopic polymeric network. With respect to extent of polymerization, both the coefficient of viscosity, η, and the elastic modulus, E, show power law dependences on the distance from the transition threshold.1) The static properties are then characterized by the connectivity transition and their description in terms of a percolation transition is in fact well known and widely accepted, with the percolation model describing the critical behaviour of static properties.1,2)

The dynamics at the sol-gel transition have been widely discussed and intensively investigated. They are characterized by a complex relaxation behaviour, showing a widening of the distribution function of relaxation times at the transition threshold and typically non-exponential decay.3-7) They eventually present some interesting analogies with the dynamics at the glass transition, but, in gelation, the relaxation process and the dramatic change in viscoelastic properties are actually controlled by the growth of connectivity.

The critical behaviour of viscoelastic properties has also been intensively debated. The experimental results for the viscosity critical exponent, κ, are quite scattered, ranging from

CCC 1022-1360/00/$ 17.50+.50/0

≈ 0.7 as measured in diisocyanate/triol systems and PDMS,[8,9] to ≈ 1.5 in epoxy resins.[10] In addition, different values for this critical exponent are obtained by applying different theoretical models. Within the Rouse model, one obtains $\kappa = 2\nu - \beta$, expressed in terms of the critical exponent, ν, for the correlation length in the system, and the critical exponent, β, describing the growth of the gel phase. When using the percolation critical exponents in three dimensions (3-D) one obtains $\kappa \approx 1.35$.[11] The de Gennes analogy with electric percolation gives κ as the critical exponent, s, of the conductivity in the random superconducting network model; $\kappa = s \approx 0.7$ in 3-D.[11,12] The elastic modulus critical exponents in the gel phase are as scattered as the experimental results: μ ranges from ≈ 1.9 measured in diisocyanate/triol[8] gels to ≈ 3 in polyesters.[13] Amongst the theoretical models, the prediction based on the de Gennes electrical analogy gives the elastic modulus critical exponent, μ, the same as the conductivity critical exponent, t, in the random resistor network model, which in 3-D is ≈ 2[14] . The bond bending model, taking into account the vectorial nature of elasticity in percolation networks, gives $\mu \approx 3.7$.[15] On the other hand, by evaluating the entropic elasticity term as the contribution of percolating clusters to the elastic free energy, one obtains $\mu = d\nu$, with $\mu \approx 2.64$ in 3-D.[16]

The Percolation Dynamic Model

In order to study the dynamics at the sol-gel transition we have recently introduced a percolation dynamic model that associates a dynamics with the percolation clusters. We consider a sol of tetrafunctional monomers, characterized by the monomer density, p, and the probability of bond formation, p_b. In terms of these two parameters the static properties present a percolation transition and a phase diagram can be determined. We consider the case of strong gelation, i.e., gelation with permanent bonds being formed. The dynamics are simulated by the bond fluctuation model (BFM):[17] the monomers move via random local movements constrained by excluded volume interactions and the self-avoiding walk (SAW) condition. As a consequence, there is a maximum bond length allowed during the dynamic evolution of the system.

We have studied the model via numerical simulations on a cubic lattice.[18] The BFM can easily be expressed in a lattice algorithm: a monomer occupies an elementary lattice cell, two occupied cells cannot share common sites and the dynamic constraints produce a finite set of

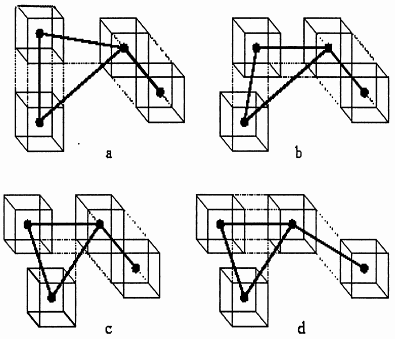

Fig. 1: A selection of four different possible configurations at different times for a cluster formed by four monomers, according to the BFM.

allowed bond lengths. An example of a possible dynamic evolution of a cluster of four monomers is shown in Fig. 1.

The numerical simulations have been performed on the CRAY-T3E system of CINECA. We have considered lattices of size L ranging between 16 and 40 lattice units and all the data have been averaged over a sample of ≈ 30 systems with different initial site and bond configurations. We have analysed the diffusion properties of the percolation clusters of different sizes at different transition stages of our model. We have examined the mean-square displacement of the center of mass and we have calculated the diffusion coefficients from the long-time diffusive behaviour. In fact as the gel point is approached, the sol becomes a complex viscoelastic medium, constituted of the solvent and percolation clusters. As the mean cluster size diverges at the percolation threshold a self-similar structure is formed characterized by the diverging coefficient of viscosity, η. Consider a probe of size R diffusing in such a medium. As long as $R >> \xi$ (where ξ is the percolation correlation length in the system), the diffusion coefficient $D(R)$ is described by the Stokes-Einstein relation $D(R) \sim 1/R^{d-2}\eta$, where d is the dimensionality. In general, for a probe of any size R, it is reasonable to assume that it will actually diffuse in the medium composed of the solvent and percolation clusters of size $r \leq R$, due to the much longer relaxation times of the very large clusters. This again can be expressed using the Stokes-Einstein relation $D(R) \sim 1/R^{d-2}\eta(R)$, with $\eta(R)$ taking into account the probe size, R.[19)] At the percolation threshold p_c $\eta \sim (p-p_c)^{-\kappa}$ and the scaling behaviour $\eta(R) \sim R^{\kappa/\nu}$ is expected in order to recover η, as $R \sim \xi$. Then, at the gel point, the diffusion coefficient $D(R)$ of a probe of size R is related to the viscosity critical behaviour

$$D(R) \sim 1/R^{d-2+\kappa/\nu} \tag{1}$$

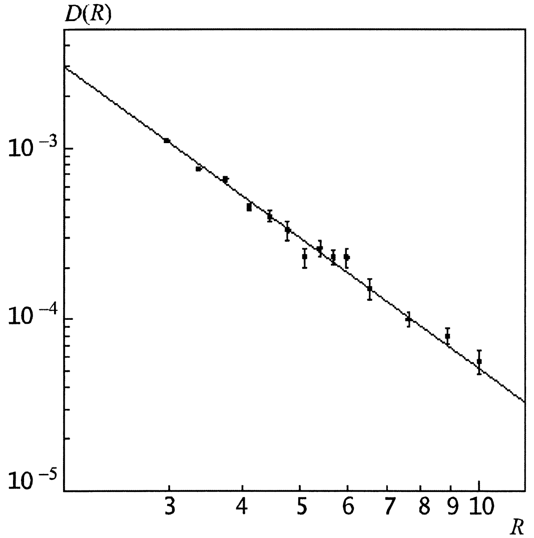

Fig. 2: The diffusion coefficients at p_c for different cluster size as a function of the clusters radius R. According to the scaling argument of eq.(1) $\kappa \approx 1.3$.

Within this scaling picture we have calculated the diffusion coefficients of clusters of radius R and from the scaling behaviour expressed through R we obtained an estimate for the viscosity critical exponent of $\kappa \approx 1.3$ (Fig. 2).

Independently, we have studied the viscosity in the system via the macroscopic relaxation time. We have calculated the time auto-correlation functions, $g(t)$, of the number of pairs of nearest neighbour monomers $\varepsilon(t)$ during the dynamic evolution

$$g(t) = \frac{<\varepsilon(t')\varepsilon(t)> - <\varepsilon(t')>^2}{<\varepsilon(t')>^2 - <\varepsilon(t)>^2} \qquad (2)$$

The functions decay to zero in the sol phase and the macroscopic relaxation time

$$\tau = \int t' g(t')\, dt' \qquad (3)$$

(calculated in the time interval where $g(t) \geq 0.01$) diverges at the gel point. The data (Fig. 3) follow a power law, giving $\kappa \approx 1.31 \pm 0.05$. This result agrees with the value determined via diffusion properties.

The value of critical exponent, κ, agrees well with some experimental results.[9,10)] It is not compatible with the prediction based on the electrical analogy, whereas it is in very good agreement with the value obtained with the Rouse model. This result may then support the idea that the hydrodynamic interactions and entanglements, which are completely neglected in the Rouse description, do not affect significantly the macroscopic time-scale behaviour of the system at the gel point.[18)]

As the gel point is approached, the time autocorrelation functions, $g(t)$, clearly show a non-exponential decay and their long-time behaviour is well fitted by the stretched exponential dependence, $e^{-(t/\tau_0)^\beta}$, with $\beta \approx 0.3$ (Fig. 4). This behaviour of the relaxation functions is considered typical for complex materials and usually interpreted in terms of a very broad distribution of relaxation times, with eventually an infinite number of them. It is in fact observed in many different gelling systems.[4-7]

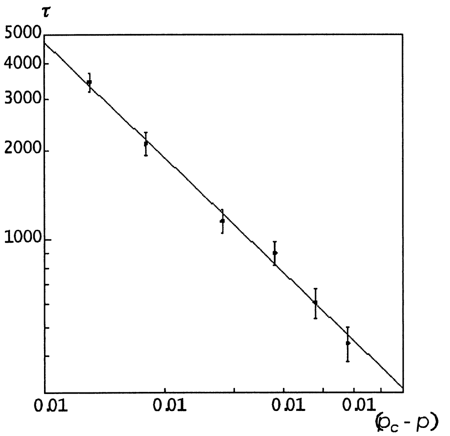

Fig. 3: The characteristic integral time τ (eq.(3)) as a function of $(p_c - p)$. The power law fit yields $\kappa \approx 1.31 \pm 0.05$.

In order to study the elastic response in the growing gel phase, we have calculated the fluctuation, Δ, in the motion of the percolating clusters center of mass.[18-20] This quantity is expected to grow as the transition threshold is approached from the gel side and the critical exponent describing this growth is directly related to the critical exponent of elastic modulus. Using the hard-wall boundary condition in the numerical simulation, we have calculated Δ as the long-time plateau value of the mean-square displacement of the center of mass of the percolating cluster, approaching the transition threshold from the gel phase (Fig. 5). The data we have obtained show that close to the percolation threshold $<\Delta R^2(t)>$ grows according to a power law. The results in 2-D and 3-D systems show very good agreement with the prediction[16] $\mu \sim d\nu$, which is supposed to express the

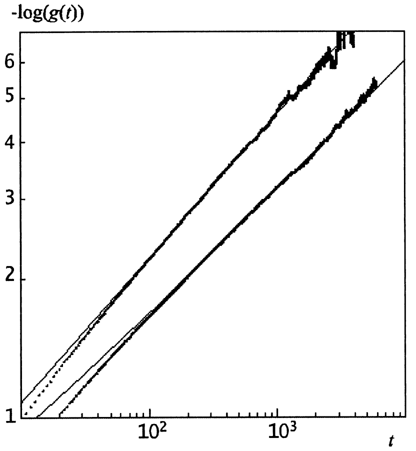

Fig. 4: Long-time tail of the time autocorrelation functions, $g(t)$. The data are well fitted by a stretched exponential decay. The two curves refer to the monomer density p=0.66 (bottom) and p=0.69 (top).

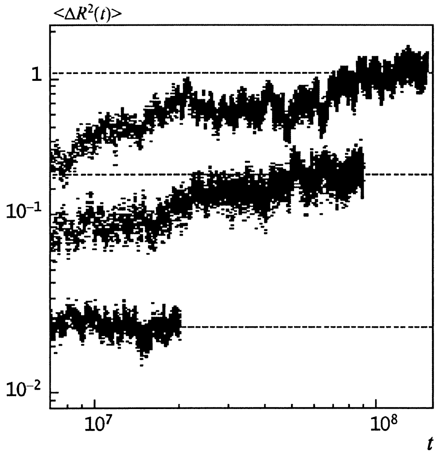

Fig. 5: The mean square displacement of the center of mass of the percolating cluster $<\Delta R^2(t)>$ in a 2-D system at different $p>p_c$ as a function of time. The dotted lines indicates the extrapolated value of $<\Delta R^2(t)>$, growing as the gel point is approached.

importance of entropic contribution to the elasticity at the gel point.$^{20)}$ It is worth noticing that we have not associated any potential energy with the polymer bonds and the elastic response of the system in the gel phase is actually entropic in origin. This result also does not agree with the prediction based on the electrical analogy.

It is worth mentioning that in the frequency dependent experiments, the complex viscoelstic modulus, G, is studied as a function of frequency, ω. In the high frequency regime, $G(\omega)\approx\omega^{\delta}$ is expected$^{2,21)}$ with $\delta=\mu/(\mu+\kappa)$. The experimental value for this exponent is $\approx$ 0.7 found in many different gelling systems.$^{8\text{-}10)}$ In this case, the exponent derived from the electrical analogy agrees well with the experimental value. The exponent determined using our model is $\approx$ 0.67, again in good agreement with experiment.$^{20)}$

Conclusions

The model we have introduced for the study of dynamics at the sol-gel transition is essentially based on percolation, excluded-volume interactions, the SAW condition and a wide variety of conformational changes. With these ingredients, the model reproduces many relevant aspects of the transition. It is suited for study of the critical behaviour of viscoelastic properties and the resulting critical exponents agree with some experimental results. Our model also shows a complex dynamic behaviour close to the transition threshold. It is characterized by a non-exponential relaxation process with the presence of a stretched exponential decay, as is acutally observed in many gelling systems. It can also easily be extended to study other aspects of gelation phenomena.

Acknowledgments

The authors acknowledge partial support from the European TMR Network-Fractals c.n.FMRXCT980183. This work was also supported by the INFM Parallel Computing, by the INFM PRA-Hop 1999, and by the European Social Fund.

References

1. P.J.Flory, *Principle of Polymer Chemistry* Cornell University Press, Ithaca (1953); P.G. de Gennes, *Scaling Concepts in Polymer Physics* Cornell University Press, Ithaca (1980)
2. M.Adam, A.Coniglio, D.Stauffer *Adv. in Polymer Sci.* **44**, 103 (1982)
3. M.Doi, S.F.Edwards *The Theory of Polymer Dynamics* Clarendon Press, Oxford (1986); J.Ferry *Viscoelastic Properties of Polymers* Wiley, New York (1980)
4. J.E.Martin, J.P.Wilcoxon, J.Odinek *Phys.Rev.A* **43**, 858 (1991)
5. F.Ikkai, M.Shibayama *Phys.Rev.Lett.* **82**, 4946 (1999)
6. T.Norisuye, M.Takeda, M.Shibayama *Macromolecules* **31**, 5316 (1998)
7. S.Z.Ren, C.M.Sorensen *Phys.Rev.Lett.* **70**, 1727 (1991)
8. M.Adam, M.Delsanti, D.Durand, G.Hild, J.P.Munch *Pure Appl.Chem.* **53**, 1489 (1981)
9. M.Adam, D.Lairez, M.Karpasas, M.Gottlieb *Macromolecules* **30**, 5920 (1997)
10. R.H.Colby, J.R.Gillmor, M.Rubinstein *Phys.Rev.E* **48**, 3712 (1993)
11. P.G.de Gennes *C.R.Acad.Sci.(Paris)B* **286**, 131 (1978)
12. J.Kertesz *J.Phys.A* **16**, L471 (1983)
13. R.H.Colby, B.K.Coltrain, J.M.Salva, S.M.Melpolder in *Fractal Aspects of Materials: Disordered Systems*, A.J.Hurd, D.A.Weitz, B.B.Mandelbrot (Eds.), Material Research Society, Pittsburgh, PA, 1987
14. P.G.de Gennes *J.Phys.Lett.* **37**, L1 (1976)
15. S.Feng, P.Sen *Phys.Rev.Lett.* **52**, 1891 (1984)
16. A.Coniglio, M.Daoud *J.Phys.A* **14**, L306 (1981)
17. I.Carmesin, K.Kremer *Macromolecules* **21**, 2819 (1988)
18. E.Del Gado, L.de Arcangelis, A.Coniglio *J.Phys.A* **31**, 1901 (1998); E.Del Gado, L.de Arcangelis, A.Coniglio *Europhys.Lett.* **46**, 288 (1999); E.Del Gado, L.de Arcangelis, A.Coniglio *Eur.Phys.J.E* **2**, 359 (2000)
19. J.E.Martin, A.Douglas, J.P.Wilcoxon *Phys.Rev.Lett.* **61**, 2620 (1988)
20. E.Del Gado, L.de Arcangelis, A.Coniglio *in preparation*
21. M.Daoud *J.Phys.A* **21,** L973 (1988)