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Viscoelasticity near the Sol−Gel Transition†

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ABSTRACT: We reconsider the exponents s and μ that characterize the behaviors of the viscosity and the elastic modulus near the Sol−Gel transition. This is done by studying the dynamics of the elastic chain that connects neighboring nodes. We assume that the characteristic time for the latter is the same as for the whole cluster. Assuming that the elastic chain has a motion similar to that of a linear chain in a melt enables us to get a simple relation between both exponents, s and μ. This allows us to provide a unified approach to the calculation of both s and μ. We find that if one assumes that the elastic chain carries an energy of the same order as the thermal energy kT, $s = \nu - \beta/2$, where ν and β are the exponents for the mesh size and the gel fraction, respectively. This relation was conjectured by Kertesz some years ago. On the other hand, if one assumes that the elastic chain is stretched, and has an energy larger than kT, one recovers the de Gennes result, $s = 2\nu - \beta$.

I. Introduction

The sol to gel transition has been continuously studied these past few years,[1−6] and the static properties of the branched polymers that constitute the sol are to some extent well understood. Their fractal properties were studied by radiation scattering experiments.[7−10] In many cases, percolation was shown to provide an adequate description of the wide polydispersity in molecular masses near the gel point. We will assume in what follows that percolation provides an adequate description of the synthesis of the randomly branched polymers. The dynamic properties on the other hand are much more controversial, and several approaches[11−16] were given to tentatively explain the experimental observations concerning both the zero frequency behaviors of the viscosity η and of the elastic modulus E, and the frequency dependences of various properties. It was shown that a wide dispersion exists also in the distribution of relaxation times. The latter was shown to be fractal, and to decrease as a power law[17,18] with an index that depends on the exponents s, which characterizes the divergence of η in the vicinity of the gelation threshold in the sol phase, and μ, which describes the vanishing of E as the threshold is approached from above, in the gel region. These indices were calculated first by de Gennes[11,12] and then by others using various assumptions. As a result, several values are predicted, and some are indeed observed. In all this previous work, the viscosity and the modulus were assumed to be independent variables. In this paper, we would like to give a single, simple, and somewhat unifying approach to these estimations, which allows us to recover the various results with a simple model. To do this, we will consider the motion of the elastic chain. This is the shortest path that links the closest nodes, or elastically active links.[10,18] The latter are those junction points that are connected to infinity in the gel. The elastic path was considered by de Gennes in his study of the elastic modulus of the gel. In what follows, we will assume that it is possible to extend this notion of elastic path to large, but finite clusters. Although it is possible to define several such paths for a large but finite branched polymer, it is possible to select one of these, and to follow its motion with time. As the cluster moves, so does the elastic path. The longest time for the cluster is identical to the one for the elastic chain: the time that is required for instance for the center of gravity of the cluster to diffuse on a distance of the order of its radius of gyration is the same as the one that is required for the elastic chain to do the same thing. Similarly, if one considers the gel, the largest time to relax any applied constraint is the same as the one to relax the corresponding constraints applied to the elastic chain. As we will see, this provides an extra relation between the exponents s and μ and allows for the calculation of both exponents. In the following, we accept that gelation is correctly described by percolation. We will first recall the results concerning the distribution of characteristic times. Then we will recall the various results about the estimations of the exponents s and μ. The elastic chain is introduced in this part. We will make several assumptions about the motion of this elastic chain in the final part, to see the implications for the values of the viscoelasticity exponents.

II. The Distribution of Times

We consider bond percolation. All sites on a d dimensional lattice are occupied. Bonds between nearest neighbors are present at random with probability p. The sites are supposed to describe the monomers, and the bonds, the chemical bonds. In this description, which was given long ago by Flory[20] and by Zimm and Stockmayer,[21] the clusters are the branched polymers. The major difference between their work and percolation[22] is that closed loops are taken into account by the latter, whereas earlier theories neglected them. Below a threshold p_c, only finite clusters are present. They constitute the sol. Above the threshold, in addition to the sol, there exists an infinite cluster that is the gel. Whereas a viscous solution, with diverging viscosity is present below the threshold, the gel provides an elastic modulus above it. The various properties of the sol may be described by a wide, fractal, distribution of molecular weights. In the following, we are interested in the dynamic properties of the sol. These are related to two quantities, namely the viscosity η of the sol, and the elastic modulus E of the gel.

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The vicinity of the gelation threshold is characterized by a divergence of the viscosity for $p < p_c$, on the sol side. Above p_c, the modulus is vanishingly small and increases as one get farther from p_c. Let $\epsilon = p - p_c$ be the distance to the threshold. Two exponents were defined to characterize the variations of η and E:

$$\eta \sim \epsilon^{-s} \tag{1}$$

and

$$E \sim \epsilon^{\mu} \tag{2}$$

These relations are valid at zero frequency. For nonvanishing frequencies ω, it is possible to write the complex modulus or the complex viscosity in the following scaled form:[23]

$$\bar{E}(\omega) \equiv E(\omega) + j\omega\, \eta(\omega) \sim \epsilon^{\mu} f(j\omega\epsilon^{-s-\mu}) \tag{3a}$$

or, equivalently

$$\bar{\eta}(\omega) = \bar{E}(\omega)/j\omega \sim \epsilon^{-s} g(j\omega\epsilon^{-s-\mu}) \tag{3b}$$

where $j = \sqrt{-1}$. The functions $f(x)$ and $g(x)$ are scaling functions with known asymptotic behaviors.[23,24] They are analytical for small arguments, and behave as power laws for large values of x. The latter point was checked experimentally,[23] and it was found that the ratio $\mu/(s + \mu)$ has a value approximately equal to 0.7.

The distribution $H(\tau)$ of relaxation times is related to the complex viscosity by a simple transformation:[24]

$$\bar{\eta}(\omega) = \int \frac{H(\tau)}{1 + j\omega\tau}\, \mathrm{d}\tau \tag{4}$$

Using relations 3b and 4, one finds the following scaled form for the distribution of relaxation times:[18]

$$H(\tau) \sim \tau^{-\mu/(s+\mu)}\, h(\tau/T_z) \tag{5}$$

where T_z is the longest relaxation time and is already present in relation 3:

$$T_z \sim \epsilon^{-s-\mu} \tag{6}$$

Note that the distribution of times cannot be described only by the longest time T_z, but that at least two different times are needed. If one calculates the normalized moments of the distribution, one finds two different divergences. In addition to T_z, there is a second diverging time. This may be seen directly in relation 4, which shows that there is a time that diverges as the viscosity:

$$T_1 \sim \epsilon^{-s} \tag{7}$$

All the diverging times behave either as T_1 or as T_z. The above discussion shows that all rheological properties of a sol or a gel close to the threshold are related to the exponent s and μ, so that it is important to know their exact values. This is discussed in the next section.

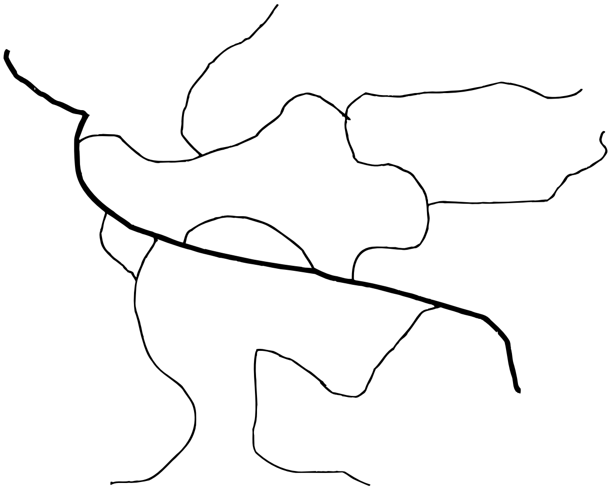

Figure 1. Sketch of an elastic path, made of N_s units, in a branched polymer with N monomers.

III. The Exponents

The exponent μ of the elastic modulus was calculated in two different ways. The most direct one was given by Coniglio et al.,[25] who argued that the elastic energy F_E per unit volume has an entropic origin and is directly related to the density of nodes. The latter are the elastically active sites, which are connected to infinity in a gel. In the critical region, there is one such nodes in a volume with linear dimension the connectedness length ξ of percolation. Thus

$$F_E \sim \xi^{-d} \sim \epsilon^{-\nu d} \tag{8a}$$

where d is the dimension of space and ν the exponent of the connectedness length. This leads to

$$\mu = \nu d \tag{8b}$$

This may be understood by assuming that every node carries an energy on the order of the thermal energy or that the elastic chain to be defined below has this energy. A different result was obtained by de Gennes,[12] who made another assumption. In his approach, he introduced the notion of an elastic chain between neighboring nodes. His argument is that such chain is elongated, so that every node carries an extra energy which may be calculated. Let us remember that the mass between two nodes in the gel is of the same order as the largest mass N_z in the sol. This is related to the characteristic distance ξ by introducing the fractal dimension D_p:

$$N_z \sim \xi^{D_p} \tag{9}$$

It is possible to introduce an elastic path between nodes, as shown in Figure 1. This may be generalized to large finite clusters. This is a linear chain made of N_s units, and has, by construction, the same dimension ξ as the cluster. The number N_s of units was calculated by using a Flory theory[26,27] in the following way: The free energy F of the elastic chain is

$$F = \frac{\xi^2}{N_s} + \frac{N_S N_Z}{\xi^d} \tag{10}$$

where the first term is the usual elastic energy of a linear chain made of N_s units. The second one is the interaction term and expresses that the N_S units of the elastic chain interact with all the N monomers of the cluster. Minimizing relation 10 with respect to ξ leads to

$$N_S{}^2 \propto \frac{\xi^{d+2}}{N_Z} \sim \xi^{d+2-D_P}$$

where we used relation 9.

Introducing an exponent $\bar{\varsigma}$ for the variation of Ns with ξ, that is the fractal dimension of the elastic chain

$$N_S \sim \xi^{\bar{\varsigma}} \tag{11a}$$

we find:

$$\bar{\varsigma} = (d + 2 - D_p)/2 \tag{11b}$$

The fractal dimension of the percolation clusters was shown to be, within a Flory approximation[28]

$$D_p = (d + 2)/2 \tag{12}$$

Using the last two relations, we finally get

$$\bar{\varsigma} = (d + 2)/4 \tag{13}$$

The latter result shows that the elastic chain is more extended than in a good solvent, if it were free. Note however that this extension is much smaller than what happens if a chain is stretched by a force for instance. In the latter case, there would be a linear relation between the size and the length. Equation 10 also shows that there is an elastic contribution to the free energy because the elastic chain is extended, if we accept the Flory evaluation for F, the minimized value of the energy is

$$F \sim \frac{\xi^2}{N_S} \sim \xi^{2-\bar{\varsigma}}$$

Therefore, because there is one such elastic chain per unit volume, the free energy per unit volume is $\xi^{2-d-\bar{\varsigma}}$, and we get, instead of eq 8b for the elasticity exponent

$$\mu = \nu(d - 2 + \bar{\varsigma}) = \nu\,(5d - 6)/4 \tag{14}$$

where the first equality is general and is de Gennes' result and the last term in eq 14 is the Flory approximation to the value for μ. Note also that if we assume that the right value for the minimized free energy is not given by the Flory approach, but is of order kT, we recover the Coniglio et al. result.

In a different, and completely independent approach, the exponent s was determined by de Gennes[11] by using an analogy with the normal-superconductor transition. He found

$$s = 2\nu - \beta \tag{15a}$$

A conjecture was made by Kertesz[29] by comparing the experimental values with the previous result. This led him to assume, instead of relation 15a

$$s = \nu - \beta/2 \tag{15b}$$

In the following, we would like to give a simple argument leading to these last two results by following the motion of the elastic chain that was considered above. If one considers the gel, it is convenient to consider the relaxation of the gel and that of the elastic chain when a constraint is applied or removed. Then, the time that is needed to relax the structure of the mesh is the same as that for the elastic chain to relax: both structures are intimately related to each other. It may also be convenient to consider the largest finite clusters. These are made of N_z units, and have a linear dimension ξ. They have roughly the same characteristics as the largest mesh of the gel. We also expect the characteristic times of the clusters and of the gel to be of the same order. For these large clusters, it is possible to define a shortest path (SP) made of N_s elements, although this might not be unique. Equations 10 and 11 relating the numbers of elements in the cluster and the SP are valid. By construction, the SP has same radius as the cluster. It also has the same relaxation time: the time that is needed for both the cluster and the SP to diffuse over a distance ξ are identical. This may be used to get an extra relation between the exponents s and μ. The most direct assumption that may be made about the dynamics of the SP is that it has a motion very similar to what is present for a linear chain in a dense solution, for instance a reptation motion.[3] This is justified by the fact that the medium is dense. It implies that the longest time T_R varies as

$$T_R \sim N_s{}^3 \tag{16}$$

Using relation 11, we get

$$T_R \sim \xi^{3\bar{\varsigma}}$$

Comparing the latter equation and relation 6, we obtain

$$\bar{s} + \bar{\mu} = 3\bar{\varsigma} \tag{17}$$

with the Flory estimate for $\bar{\varsigma}$ given by eq 13. In the previous equation, we introduced $\bar{s} = s/\nu$ and $\bar{\mu} = \mu/\nu$.

Using the latter relation, it is then possible to get the values for the viscosity exponent s corresponding to both assumptions for the elasticity exponent μ.

From eqs 8b and 17 we obtain

$$\bar{s} = (6 - d)/4 \approx 1 - \bar{\beta}/2 \tag{18a}$$

On the other hand, using the de Gennes result, eq 14 together with eq 17, we get

$$\bar{s} = (6 - d)/2 \approx 2 - \bar{\beta} \tag{18b}$$

Thus, within a Flory approximation, we find that both estimates by de Gennes and by Kertesz for s correspond to the two different results discussed above for the elasticity exponent, if we assume a the same type of motion for the elastic chain as for a linear polymer in a melt, for instance reptation. Let us note that this result is also valid if we assume tube renewal for the motion of the elastic chain: relation 17 remains valid if such assumption is made.

Note that the assumption that the elastic chain has a motion similar to that of a linear chain in a melt does not imply that the branched chains do have such motion: there is no reptation for the branched polymers. This may be seen for instance if we come back to eq 6 for the longest time. This may be written in a different form

$$T_z \sim \xi^{\bar{s}+\bar{\mu}} = \xi^{\bar{s}+d-2}\ \xi^{2-d+\bar{\mu}} \sim \xi^{2-d+\bar{\mu}}/D$$

where D is a diffusion coefficient obeying the usual $D = 1/\eta R^{d-2}$ law. In the Coniglio et al. approach, the numerator is merely ξ^2, leading to a classical diffusion law for the large branched polymers. We also note that the motion of polydisperse branched polymers in the reaction bath is faster than that of linear chains with the same number of units: combining eqs 12, 13, and 16, we get

$$T_z \sim {N_s}^3 \sim {N_z}^{3/2}$$

We finally would like to mention a surprising result, which may be accidental. If we forget about eq 16 and accept the minimal idea that the characteristic time of the elastic chain is identical to that of the cluster, relation 6, and that the molecular weight N_s of the elastic chain is related to the mass of the cluster by eq 11, we find, instead of eq 16, the following relation between the characteristic time and mass:

$$T_z \sim {N_s}^{(s+\mu)/\varsigma}$$

Using the accepted experimental values of the exponents in ref 19, namely $\bar{\varsigma} \approx 1.25$, $\nu \approx 0.9$, $s \approx 0.8$, and $\mu \approx 3$, one finds a value for the latter exponent very close to the 3.4, rather than 3, that is the one that is usually observed in linear polymer melts. Although this value might be purely accidental, it might mean that a melt may, to some extent, be considered as a system close to a sol–gel transition, where entanglements play the role of temporary cross-links.

Finally, we note that the second, shorter, time, T_1, should also appear in the relaxation of the SP. Using eqs 7 and 18, we get $T_1 \sim {\rm N}_s{}^{\bar{s}}/\bar{\zeta}$, with $\bar{s} = {}^6/_5$ and ${}^3/_5$, respectively, in the de Gennes and Kertesz approximations, relation 18.

Conclusion

We considered the rheological properties of a system close to its sol–gel transition. We assumed that the latter may be described by percolation, and that one may always define an elastic- or shortest-path (SP) for the large but finite clusters. To describe the longest relaxation time in this system, we assumed that the characteristic time for the cluster is proportional to the one for the elastic path: when a large but finite cluster diffuses over a distance that is on the order of its radius, so does the shortest path in this cluster. Similarly, the rate at which the gel relaxes should be the same as that for the shortest path. We evaluated this time by considering the motion of the elastic path: because the system is dense, we assumed that such a linear chain has a reptation motion. This assumption provides a relation between the exponents s and μ characterizing respectively the viscosity and the elastic modulus in the vicinity of the transition. This in turn allows us to have a unified approach to the determination of both exponents. Assuming that the SP has thermal energy leads to $\bar{s} = (2 - d + D)/2$, and $\bar{\mu} = d$, where d and D are respectively the dimension of space 3 and the fractal dimension of the clusters. Assuming that the SP carries an extension energy larger than kT, leads to the de Gennes results $\bar{s} = (2 - d + D)$, and $\bar{\mu} = d - 2 + \bar{\varsigma}$, where $\bar{\varsigma}$ is the fractal dimension of the SP.

We conclude by noting that it would certainly be very interesting to consider the characteristic times of the elastic path by computer simulations.

References and Notes

(1) Dusek, K. In *Physics of finely divided matter*; Boccara, N., Ed.; Springer Proc. Phys. 5; Springer: Berlin, 1985.
(2) Stauffer, D. *J. Chem Soc., Faraday Trans. 2* **1976**, *72*, 1354.
(3) de Gennes, P. G. *Scaling concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(4) Daoud, M.; Martin, J. E. In *The fractal approach to the chemistry of disordered systems*; Avnir, D.; Ed.; J. Wiley: New York, 1989.
(5) Adam, M.; Lairez, D. In *Physical properties of polymeric gels*; Cohen Addad, J. P., Ed.; J. Wiley: New York, 1996.
(6) Bastide, J.; Candau, S. J. In *Physical properties of polymeric gels*; Cohen Addad, J. P., Ed.; J. Wiley: New York, 1996.
(7) Schosseler, F.; Leibler, L. *J. de Physique Lett.* **1984**, *45*, 501.
(8) Bouchaud, E.; Delsanti, M.; Adam, M.; Daoud, M.; Durand, D. *J. Phys. Lett.* **1986**, *47*, 1273.
(9) Colby, R. H.; Rubinstein, M.; Gillmor, J. R.; Mourey, T. H. *Macromolecules* **1992**, *25*, 7180.
(10) Munch, J. P.; Delsanti, M.; Durand, D. *Europhys. Lett.* **1992**, *18*, 577.
(11) de Gennes, P. G. *C. R. Acad. Sci. (Paris)* **1980**, *291*, 17.
(12) de Gennes, P. G. *J. Phys. Lett.* **1976**, *37*, 61.
(13) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev.* **1989**, *A39*, 1325.
(14) Colby, R. H.; Gillmor, J. R.; Rubinstein, M. *Phys. Rev.* **1993**, *E 48*, 3712.
(15) Adam, M.; Delsanti, M. In *New trends in Physics and Physical Chemistry of polymers*; Lieng-Huang Lee, Ed.; Plenum Press: New York, 1989.
(16) Devreux, F.; Boileau, J. P.; Chaput, F.; Malier, L.; Axelos, M. A. V. *Phys. Rev.* **1993**, *E 47*, 2689.
(17) Clerc, J. P.; Giraud, G.; Laugier, J. M.; Luck, J. M. *J. Phys.* **1986**, *A19*, 3153.
(18) Daoud, M. *J. Phys.* **1988**, *A21*, L973.
(19) Havlin, S.; Ben Avraham, D. *Adv. Phys.* **1987**, *36*, 695.
(20) Flory, P. J. *Principles of polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(21) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(22) Stauffer, D. *Introduction to percolation theory*; Taylor and Francis: London, 1985.
(23) Durand, D.; Delsanti, M.; Adam, M.; Luck, J. M. *Europhys. Lett.* **1987**, *3*, 297.
(24) Ferry, J. D. *Viscoelastic properties of polymers*; J. Wiley: New York, 1980.
(25) Coniglio, A.; Daoud, M. *J. Phys.* **1981**, *A14*, L301.
(26) Coniglio, A.; Family, F. *J. Phys. Lett.* **1985**, *46*, 9.
(27) Roux, S. *C. R. Acad. Sci. (Paris)* **1985**, *301*, 367.
(28) Isaacson, J.; Lubensky, T. C. *J. Phys.* **1981**, *42*, 175.
(29) Kertesz, J. *J. Phys. A* **1983**, *16*, L471.

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