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Abstract. Branched polymers are most usually synthesized in the vicinity of a sol–gel transition and are very polydisperse. The number distribution was shown experimentally to be the same as in percolation. This may be described by two characteristic masses, N_z and N_w, that diverge with different exponents. Similarly, one finds that there is a continuous distribution of relaxation times, varying as a power law cut-off at large times by an exponential decay. In the reaction bath, this distribution is related to the viscoelastic properties. In a dilute solution, it may be related to the distribution of masses. In both cases, two diverging times may be defined. We review the properties of these distributions of relaxation times, and consider the consequences on the relaxation of branched polymers in the reaction bath and in solution.

1. Introduction

Much attention has been paid recently to the properties of randomly branched polymers and gels close to the gelation threshold [1–15]. This is partly related to the intrinsic polydispersity that is present in such systems. Indeed, it was shown experimentally that the synthesis of most of these systems may be described by percolation. Such description was initiated by Flory and Stockmayer [1] some years ago, in the loopless approximation, and extended more recently by Stauffer [16] and de Gennes [3] to the critical region that is present in the vicinity of the gelation transition. One of the main results of these approaches, both theoretical [16] and experimental [6–8] is that the sol, made of finite but large polymers, contains a broad distribution of molecular weights. Such distribution is self similar [4], with smaller polymers residing in the holes of the large fractal [17] polymers. It was shown that the number distribution, that is the probability $P(N, \varepsilon)$ of finding a macromolecule made of N monomers at a distance ε from the gelation threshold, is

$$P(N, \varepsilon) \sim N^{-\tau} f(\varepsilon N^{\sigma}) \tag{1}$$

with

$$\tau = 1 + d/D_{\mathrm{p}} \tag{2}$$

where σ is a percolation exponent, d the dimension of space and D_{p} the fractal dimension

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of the polymers in the reaction bath. A polymer made of N monomers has a radius $R(N)$, with

$$N \sim R(N)^{D_p}. \tag{3}$$

The distribution equation (1) is characterized not by a single, but by two diverging masses, namely

$$N_w \sim \int N^2 P(N, \varepsilon) \, dN \sim \varepsilon^{-\gamma} \tag{4}$$

and

$$N_z \sim \frac{1}{N_w} \int N^3 P(N, \varepsilon) \, dN \sim \varepsilon^{-(\beta+\gamma)}. \tag{5}$$

Such a very broad distribution leads to measurements of effective fractal dimensions [18–20] instead of the actual ones in the static properties. For instance, the intensity $S(q)$ of scattered radiation by a dilute solution of branched polymers in the intermediate range, $R_z^{-1} \ll q \ll l^{-1}$, where l is the monomer size and q the momentum transfer, is

$$S(q) \sim q^{-D(3-\tau)} \tag{6a}$$

instead of the usual

$$S_1(q) \sim q^{-D} \tag{6b}$$

valid for a fractal with dimension D, when no polydispersity is present.

In the following, it will be shown that the relaxation spectrum in such systems is also very broad, decaying as a power-law cut-off by an exponential decay at long times. It may be characterized by two diverging times, even in a dilute solution, as we will see in section 3. In section 4 some consequences for the stress relaxation in the reaction bath, for the light scattering intensity by a dilute solution are outlined. As we shall see, changes such as stretched exponential or power-law relaxations are expected.

2. The reaction bath

2.1. Scaling

The sol–gel transition may be characterized [3] by a divergence of the viscosity η of the sol at the gelation threshold:

$$\eta \sim \varepsilon^{-s} \qquad (\varepsilon \to 0_-). \tag{7}$$

It may also be characterized by a vanishing elastic modulus E above the threshold:

$$E \sim \varepsilon^{\mu} \qquad (\varepsilon \to 0_+) \tag{8}$$

where s and μ are exponents to be discussed below. It is then possible [21] to define a complex frequency-dependent modulus $\bar{E}$ and a complex viscosity $\bar{\eta}(\omega)$ such that

$$\bar{E}(\omega) = i\omega\bar{\eta}(\omega) = E(\omega) + i\omega\eta(\omega) \tag{9}$$

where $i = \sqrt{-1}$ and $E(\omega)$ and $\eta(\omega)$ are the frequency-dependent modulus and viscosity,

respectively. Relations (7) and (8) are the zero frequency limits of both quantities. It is postulated [22–24] that the following scaled form for the complex viscosity holds

$$\bar{\eta}(\omega) \sim \varepsilon^{-s} f_{\pm}(\mathrm{i}\omega T) \tag{10}$$

where T is the largest diverging time in the system. It was shown that

$$T \sim \varepsilon^{-s-\mu} \tag{11}$$

and $f_{\pm}(x)$ is a function with known limits. Both $\bar{E}$ and $\bar{\eta}$ are response functions and may be directly related to the distribution $H(\tau)$ of relaxation times of the system [25]:

$$\bar{\eta}(\omega) \sim \int \frac{H(\tau)}{1 - \mathrm{i}\omega\tau} \, \mathrm{d}\tau. \tag{12}$$

From knowledge of the scaled form of the complex viscosity, it is possible to obtain the scaling of $H(\tau)$. We find

$$H(\tau) \sim \tau^{-\mu/(s+\mu)} h_{\pm}\left(\frac{\tau}{T}\right). \tag{13}$$

Thus one finds [26, 27] for the distribution of relaxation times a power-law decay, cut off by an exponential for times larger than T. Since the exponent in the power law is less than unity, it is possible to define two characteristic diverging times [25] for this distribution. The first one corresponds to the viscosity, as may be seen directly from relation (12) for zero frequency. More precisely, adopting a logarithmic scale, we may define the moments of the distribution as

$$M_n(\varepsilon) = \int H(\tau)\tau^n \, \mathrm{d}\ln(\tau). \tag{14}$$

Because M_0 does not diverge we have

$$T_1 \sim M_1(\varepsilon)/M_0(\varepsilon) \sim \eta \sim \varepsilon^{-s}. \tag{15}$$

Higher order moments diverge with the same exponent, and allow us to recover the longest time T that was introduced above:

$$T \sim M_3/M_2 \sim M_4/M_3 \sim \ldots \sim \varepsilon^{-(s+\mu)}. \tag{16}$$

The first test of these scaling relations was made on the frequency dependence of the modulus and is discussed below. Relation (9) shows that the high-frequency dependence of the viscosity, which is expected to be independent of the distance ε to the threshold because one is probing finite regions of space, should behave as a power of the frequency ω. For the complex modulus, this gives

$$\bar{E}(\omega) \sim (\mathrm{i}\omega)^{-\mu/(s+\mu)}. \tag{17a}$$

The latter relation implies that both the real and imaginary parts should have a power-law behaviour and that the loss angle should be constant. This was checked experimentally by several groups, with the experimental result

$$\mu/(s + \mu) = 0.70 \pm 0.05. \tag{17b}$$

2.2. Exponents

Whereas the ratio (17b) met with very large agreement among experimentalists, two sets of values for s and μ were found. These correspond to the cases where hydrodynamic

interactions are present in the reaction bath, or Zimm model, or, on the contrary where no hydrodynamic interactions are present, or Rouse model. The latter case was considered by de Gennes [28] some years ago. He showed that the viscosity diverges as

$$\eta \sim \langle R^2 \rangle_\mathrm{w} \sim \varepsilon^{-(2\nu-\beta)} \qquad (\text{Rouse}). \tag{18}$$

This allows the calculation of the exponent μ of the modulus:

$$\mu_\mathrm{r} = \nu d \qquad (\text{Rouse}). \tag{19}$$

When hydrodynamic interactions are present, the modulus was calculated in a Flory approximation by Roux [29] and Coniglio and Family [30]:

$$\mu_\mathrm{z} = \nu(d - 2 + D_\mathrm{p}/2) \qquad (\text{Zimm}) \tag{20a}$$

and Kertesz [31] conjectured

$$s_\mathrm{z} = \nu - \beta/2 \qquad (\text{Zimm}). \tag{20b}$$

The latter relation may be recovered within the Flory approximation if we accept the relation $D \sim \xi^{-1}$ in the reaction bath between the diffusion coefficient D and the size ξ of the largest polymers. Note that the two models lead to a difference in the viscosity exponents by a factor two.

We conclude this subsection by noting that the situation concerning the exact values of the exponents is not resolved at this time. If we accept the idea that two universality classes are present for the dynamical properties, then wherever the ratio $\mu/(s + \mu)$ is present, no difference appears between both cases. On the contrary, wherever any of the exponents appear a clear difference is to be observed between the classes.

3. Dilute solutions

Once the polymers have been synthesized, we assume that the distribution of masses $P(N, \varepsilon)$ is quenched. In this section we consider the case of dilute solutions, when each polymer is sufficiently far from the others so that no interference effects are present among the signals due to various polymers in the solution, and that concentration effects are only perturbations. In this case, hydrodynamic interactions [32] are clearly present, and a Zimm type of dynamics is valid. Thus for any polymer, with any mass N and radius $R(N)$ in the distribution, one has a longest time of

$$T(N) \sim R(N)^3. \tag{21}$$

Because there is a distribution of masses, one expects a distribution of times. This may be estimated in the same way as above. The intrinsic viscosity $[\eta]$ of a dilute solution was recently calculated [18, 33]

$$[\eta] \sim N_\mathrm{w}^{-3/8} \tag{22}$$

where we have used the Flory value of the fractal dimensions of a polymer in the reaction bath and in a dilute solution. From relations (21) and (22) it is possible to write down a

scaled form of the frequency-dependent viscosity and, with the same kind of transformation as above, to deduce a scaled form for the distribution of relaxation times in a dilute, polydisperse solution of randomly branched polymers. We find

$$H_d(\tau) \sim \tau^{-4/5} h(\tau/N_w^{15/8}). \tag{23}$$

As above, this spectrum is characterized by two diverging times

$$T_{d1} \sim N_w^{3/8} \tag{24a}$$

and

$$T_d \sim N_w^{15/8}. \tag{24b}$$

4. Some consequences

Several experiments were performed to check these scaling assumptions, including quasi-elastic light scattering and viscoelastic measurements.

4.1. Viscoelasticity

The frequency dependence of the complex modulus in the reaction bath was investigated by Durand *et al* [34], Rubinstein *et al* [26], Martin *et al* [33] and Axelos and Kolb [35]. As discussed above, however, the interpretation of the ratio $\mu/(s + \mu)$ (relation (17)), is not unique, and both Zimm and Rouse dynamics were used by the various groups. Direct measurements of the zero-frequency viscosity were also performed, leading their authors to estimate the exponent s. Note however that the result of these measurements depends crucially on the exact determination of the threshold. It would be extremely interesting to determine the viscosity dependence as a function of another measured variable, such as the average mass N_w for instance. Note also that these measurements rule out an $\omega^{1/2}$ dependence of the viscosity, as implied by the classical effective medium, Rouse, theory [21].

Relaxation experiments have not been attempted so far. Their results would be interesting because different regimes are present: let us consider a sample subject to an external constraint such as a force or a shear. When this constraint is released, it relaxes to equilibrium. If only one relaxation time τ is present, the relaxation process is exponential:

$$X_\tau(t) \sim e^{-t/\tau}. \tag{25}$$

Since there is a distribution of relaxation times, the process is a convolution of such relaxations. Assuming that the various modes are independent, we get

$$X(t) \sim \int \tau^{-x} H(\tau) e^{-t/\tau} \, d\tau \tag{26}$$

where we assumed that the weight of each mode has a power-law variation. For times

smaller than the longest time T, the distribution is a power law and we obtain, using relation (13)

$$X(t) \sim t^{s/(s+\mu)-x}. \tag{27}$$

For larger times, the distribution is basically an exponential, and neglecting the power-law prefactors, we have

$$X(t) \simeq \int e^{-t/\tau} \, e^{-\tau/T} \, d\tau. \tag{28}$$

Estimating the latter integral by steepest descent, we obtain

$$X(t) \simeq e^{-(t/T)^{1/2}}. \tag{29}$$

Thus one finds a power law relaxation for times shorter than T, followed by a stretched exponential for larger times.

4.2. Light scattering

In dilute solutions, where no interactions are present among polymers, it was recently argued that relaxation of electric birefringence [36] leads to stretched exponential behaviour for large times, for the same reason as above: only the exponentially few very large polymers still relax for long times. Another set of experiments was performed for quasi-elastic light scattering. The results may be summarized as follows [37].

(i) For very dilute solutions, an exponential decay is observed.

(ii) Increasing the concentration, this simple exponential becomes a stretched exponential, $\exp[-(t/T)^{\beta}]$, with an exponent β which decreases when the concentration is increased, and seems to reach an asymptotic value of the order of $\frac{1}{3}$ in the semi-dilute regime.

(iii) For still higher concentrations, a power-law decay appears and gradually occupies the observation range.

Calculations of the scattered intensity $l(q, t)$ [38] in the dilute regime lead, in the very low-q limit, to a diffusive limit, with

$$l(q, t) = CN_w \exp(-D_z q^2 t) \tag{30}$$

where

$$D_z = N_w^{-5/8} \tag{31}$$

is the effective diffusion coefficient and has an exponent that takes into account both the fractal dimension of a single polymer and the polydispersity of the system. This behaviour was observed recently by Candau *et al* [39].

For $qR_z \ll 1$ and $D_z q^2 t \gg 1$, it was found

$$l(q, t) \sim (CN_w/D_z q^2 t) \exp(-D_z q^2 t). \tag{32}$$

In the experimental range, this may be interpreted as a pseudo-stretched exponential decay with an exponent 0.8.

Finally, when the concentration is varied the results are more complicated, and one may consider that the problem is still open.

5. Conclusions

Whereas there is large agreement that the dynamic properties of randomly branched polymers are characterized by a very broad distribution of relaxation times, the exact exponent of the power-law decay is still under discussion. More precisely, it is not clear at this time that only one universality class is present in the reaction bath for all systems, whereas this is accepted for dilute solutions. Such a broad distribution leads to non-exponential relaxations, such as power laws or stretched exponentials as discussed above. However, more experimental results are clearly needed to resolve this fascinating and practically very important question.

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