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LETTER TO THE EDITOR

Dynamics of branched polymers in the reaction bath

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Abstract. We consider the dynamics of a polydisperse sol made of randomly branched polymers near the gelation threshold. Assuming that the distribution is that of percolation, we review various possible hydrodynamic interactions, namely the Rouse limit, where no backflow is present, and the Zimm limit, where hydrodynamic interactions are present. In the latter case, we recover a recent conjecture by Kertész for the divergence of the viscosity. In the former case, we recover the de Gennes-Stephen results. We discuss the viscoelastic behaviour at short timescales.

The dynamical properties of large clusters in the vicinity of the percolation threshold have been widely studied in the last few years. The propagation of excitations along these fractal structures was considered (Alexander and Orbach 1982, Rammal and Toulouse 1983, Gefen *et al* 1983) and a calculation of the exponent s of the viscosity was given by Stephen (1978) and de Gennes (1980a). However, the latter does not agree with most experimental results which lead to a value equal to half of the calculated one. Recently, Kertész (1983) made the conjecture that $s = \nu - \frac{1}{2}\beta$ by considering the capacitance between clusters rather than the polarisability of the clusters. Such differences were also discussed by Coniglio and Stanley (1984) and Bunde *et al* (1985) in terms of 'termite' versus 'ant' diffusion. In the present letter, we would like to consider the problem from the point of view of the dynamics of polymer solutions. As we shall see, this will allow us to reconcile both results within different approximations: basically, these correspond to the Rouse and Zimm approximations, where hydrodynamic interactions are either neglected or taken into account respectively (de Gennes 1979). In both cases, we may use the viscoelastic properties of polymers: if we apply a constant stress we expect for sufficiently long times, larger than a characteristic time T_z to be discussed below, a viscous behaviour characterised by a viscosity η . For shorter times, an elastic behaviour is expected, characterised by a modulus E . The crossover time T_z is related to E and η by

$$\eta = ET_z. \quad (1)$$

For scalar elasticity (Alexander 1985), the exponent t of the modulus E was conjectured by de Gennes (1976) and calculated within a Flory approximation by Family and Coniglio (1985) and Roux (1985). Their result is

$$E \sim \xi^{-\bar{t}} \quad (2')$$

with

$$\bar{t} = t/\nu = d - 2 + \frac{1}{2}D_p \quad (2)$$

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where ξ is the radius of the largest polymers, d is the dimension of space and D_p is the fractal dimension of the percolating cluster. The latter was also calculated in the same approximation (Isaacson and Lubensky 1981, de Gennes 1980b)

$$D_p = \frac{1}{2}(d + 2). \quad (3)$$

In the following, we evaluate the viscosity exponent by calculating the time T_z in different approximations.

The most direct way is to assume that there are no hydrodynamic interactions between the various polymers present in the reaction bath. This corresponds to the Rouse approximation (Stockmayer 1976). The only possible motion for any polymer then is through the propagation of local motion (or excitation) along the macromolecule itself. This was considered recently by Alexander and Orbach (1982) in the case of the infinite cluster (i.e. the gel) and Gefen *et al* (1983) for the finite clusters (i.e. the sol). The longest time is readily calculated:

$$T_z = \xi^2 / D \quad (4)$$

where ξ is the characteristic length and corresponds to the largest polymers present and D is the diffusion coefficient along the polymer. Assuming the same fractal structure for the large polymers as for the gel, we get

$$D \sim \xi^{\bar{\beta} - \bar{\tau}} \quad (5)$$

with $\bar{\beta} = d - D_p$. Combining relations (4) and (5) we get

$$T_z \sim \xi^{\bar{\tau} + 2 - \bar{\beta}} \quad (6)$$

$$\sim N_w^{15/8} \quad (d = 3) \quad (6')$$

where the weight-average molecular weight N_w is proportional to the mean cluster size and is related to ξ :

$$\xi \sim N_w^{1/(2D_p - d)} \sim N_w^{1/2}. \quad (3')$$

Using equations (1) and (6) we get

$$\eta \sim \xi^{2 - \bar{\beta}} \quad (7)$$

$$\sim N_w^{3/4} \quad (d = 3) \quad (7')$$

and thus the exponent for the divergence of the viscosity in this approximation is

$$\bar{s} = 2 - \bar{\beta}. \quad (8)$$

This expression was found by Stephen (1978) and de Gennes (1979) and does not seem to be in good agreement with experimental results for flexible polymers in the vicinity of the gelation threshold. It might be interesting to test it with more rigid structures such as silica (Schaefer 1985, Courtens *et al* 1987). Relations (2) and (7) may also be tested through the frequency dependences of the out of phase and in-phase complex modulus. We expect

$$\eta(\omega) \sim \xi^{\bar{s}} f(\omega \xi^{2 - \bar{\beta} + \bar{\tau}}) \quad (9)$$

$$\sim \omega^{-(2 - \bar{\beta}) / (2 - \bar{\beta} + \bar{\tau})} \quad (\omega T_z \gg 1) \quad (10)$$

$$\sim \omega^{-2/5} \quad (d = 3) \quad (10')$$

and, in the same way,

$$E(\omega) \sim \omega \eta(\omega) \sim \omega^{\bar{\tau}/(2-\bar{\beta}+\bar{\tau})} \quad (11)$$

$$\sim \omega^{3/5} \quad (d=3). \quad (11')$$

Finally using relations (2) and (8) we get

$$\bar{s} + \bar{\tau} = 3D_p/2 = 3(d+2)/4. \quad (12)$$

Let us now consider the opposite limit and assume that hydrodynamic interactions are present in the reaction bath between monomers. This corresponds to the Zimm limit (Stockmayer 1976, de Gennes 1979). In a Flory approximation this implies that the longest time has the following behaviour.

$$T_z \sim \xi^d \quad (13)$$

$$\sim N_w^{3/2}. \quad (13')$$

Using relations (1) and (13) we get, instead of relation (12),

$$\bar{s} + \bar{\tau} = d \quad (14)$$

which was conjectured by Straley (1980). Together with equations (2) and (3) this implies for the divergence of the viscosity

$$\bar{s} = (2-d+D_p)/2 \quad (15)$$

and thus we get instead of relation (7)

$$\eta \sim N_w^{3/8}. \quad (16)$$

Relation (15') is a conjecture made recently by Kertész and is in very good agreement with the experimental results for flexible polymers (Adam *et al* 1979, 1985). The corresponding frequency-dependent properties at high frequencies:

$$\eta(\omega) \sim \omega^{-\bar{s}/d} \sim \omega^{-1/4} \quad (\omega T_z \gg 1) \quad (17)$$

$$E(\omega) \sim \omega^{\bar{\tau}/d} \sim \omega^{3/4} \quad (\omega T_z \gg 1) \quad (18)$$

are in reasonable agreement with recent observations by Durand *et al* (1986) on polyurethane polymers close to the gelation threshold. That hydrodynamic interactions are present in the reaction bath is not really surprising since we know that, close to the gelation threshold, there is a huge number of small molecules that are able to mediate the hydrodynamic interactions. However, it should certainly be interesting to check whether more rigid systems polymerising in an already viscous solvent might cross over to a Rouse-type hydrodynamics.

Relation (13) allows us to analyse the viscoelastic behaviour of the polymers in the reaction bath. In order to do this let us consider the propagation of an information in the medium. We are immediately led to separate short times from long times. For short times, the information essentially remains on the same large cluster. For larger times, it travels between the large clusters. As mentioned above, the crossover time is T_z .

We consider the short scales first. Let us focus on a given large cluster. The information may be transmitted in two different ways.

(i) Along the large macromolecule in a Rouse-type process. As discussed above, this leads to a time

$$T_1 \sim \xi^2/D \sim \xi^{2-\bar{\beta}+\bar{i}} = \xi^{D_w}. \quad (6a)$$

(ii) A second way is via the smaller polymers interpenetrating the large one. The analysis of such motion may be done following the lines of Coniglio and Stanley (1984, hereafter referred to as *CS*). The main difference between their analysis and the present one is that, because we consider here the short-time behaviour, we do not consider the motion between large polymers but, at this stage, only those where the information is recaptured by the initial large cluster. In 'zoological' terms, we consider the motion of a termite between two points on the same large cluster through smaller polymers. In principle, this is identical in essence to the motion between large clusters, with one important difference: the termite may leave the large cluster from a large number of sites, of the same order as its size $N \sim \xi^{D_p}$.

The time to come back onto the initial cluster is the same as calculated by *CS*:

$$T' \sim \xi^{d_w} \quad (19)$$

with

$$d_w = 2 - \bar{s} \quad (20)$$

$$= (2 + d - D_p)/2 \quad (D_p > 2). \quad (20')$$

In order for the information to leave the cluster it has to visit N sites as mentioned above. Thus the total transmission time is

$$T'_1 \sim NT' \sim \xi^{D_p+d_w}. \quad (21)$$

Because of the viscoelastic behaviour, we argue that both ways are equivalent so that T_1 and T'_1 are of the same order of magnitude.

Comparing relations (6a) and (21) we find

$$D_w = D_p + d_w \quad (22)$$

$$= (2 + d + D_p)/2 \quad (D_p > 2) \quad (22')$$

where we used relation (20). Comparing relations (6a) and (22), we find

$$\bar{i} = d - 2 + d_w \quad (23)$$

$$= (3d - D_p - 2)/2 \quad (D_p > 2). \quad (23')$$

Relations (23) and (22) have not previously been reported, to our knowledge. Equation (22') reduces to the Alexander and Orbach (1982) conjecture in the Flory approximation. The consequence, as mentioned above, is that the characteristic longest time T_z is

$$T_z \sim \xi^{\bar{s}+\bar{i}} \sim \xi^d. \quad (24)$$

Note that it is much shorter than the step time T_1 that we have just discussed. In order to understand this difference, we emphasise that so far we considered one single large polymer and we neglected any transfer of information to other polymers with the same size. Following *CS*, we know that this is possible through a fraction of the N sites corresponding to the unscreened perimeter, with N_u sites. Thus the crossover time T_z is

$$T_z \sim T_1 N_u / N \quad (25)$$

with N_u the mass of the unscreened perimeter:

$$N_u \sim \xi^{d-d_w}. \quad (26)$$

Combining relations (21), (25) and (26), we recover (24). Thus we do not expect the previous analysis to hold until T_1 , but only until T_2 . For larger times, we expect the cs analysis of the motion between large polymers to hold. This corresponds to a purely viscous behaviour.

We considered two possible hydrodynamic regimes for polydisperse branched polymers in the reaction bath. In the Rouse limit, the excitations travel along the polymers. In the Zimm limit, the excitations are mediated by smaller polymers. We argued that the viscoelastic behaviour at short times corresponds to the coexistence of both processes. Assuming the characteristic times for both processes are of the same order leads to another conjecture for the exponents D_w and d_w of the random walk in both problems (i.e. the ant and the termite, respectively). We find $D_w = D_p + d_w$, with D_p the fractal dimension of the polymers. Above a crossover time $T_z \sim \xi^d$, with d the dimension of space, excitations travel between large polymers, and the pure viscous (termite) behaviour is expected. This implies that the fracton behaviour may be seen only indirectly in such systems, where hydrodynamic interactions are important. From this point of view, it should certainly be very interesting to look for systems where hydrodynamic interactions are screened. Vulcanised polymers might be candidates.

The short-time analysis leads to a second characteristic time, $T' \sim \xi^{2-s} \sim N_w^{5/8}$, below which one considers the motions of smaller polymers inside the larger ones. This may lead to interesting consequences for the dispersion relations.

Finally, we note that the short-time analysis does not hold when polymers do not overlap. This is the case for narrow fractions of the polymers we discussed, and for rigid aggregates (Meakin 1983, Kolb *et al* 1983) where the aggregates have basically the same size (Vicsek and Family 1984). In both cases there are no small polymers to mediate the interactions at short timescales.

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References

- Adam M, Delsanti M and Durand D 1985 *Macromol.* **18** 2285
 Adam M, Delsanti M, Okasha R and Hild G 1979 *J. Physique Lett.* **40** 539
 Alexander S 1985 *The Physics of Finely Divided Matter* (Berlin: Springer)
 Alexander S and Orbach R 1982 *J. Physique Lett.* **43** 625
 Bunde A, Coniglio A, Hong D C and Stanley H E 1985 *J. Phys. A: Math. Gen.* **18** L144
 Coniglio A and Stanley H E 1984 *Phys. Rev. Lett.* **52** 1068
 Courtens E, Pelous J, Phalippou J and Woignier T 1987 *Phys. Rev. Lett.* **58** 128
 de Gennes P G 1976 *J. Physique Lett.* **37** 61
 — 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
 — 1980a *J. Physique Colloq.* **41** C3
 — 1980b *C. R. Acad. Sci., Paris B* **291** 17
 Durand D, Delsanti M, Adam M and Luck J M 1987 *Europhys. Lett.* **3** 297
 Family F and Coniglio A 1985 *J. Physique Lett.* **46** 9
 Gefen Y, Aharony A and Alexander S 1983 *Phys. Rev. Lett.* **50** 77
 Isaacson J and Lubensky T C 1980 *J. Physique Lett.* **41** 469

- Kertész J 1983 *J. Phys. A: Math Gen.* **16** L471
Kolb M, Botet R and Jullien R 1983 *Phys. Rev. Lett.* **51** 1123
Meakin P 1983 *Phys. Rev. Lett.* **51** 1119
Rammal R and Toulouse G 1983 *J. Physique Lett.* **44** 43
Roux S 1985 *C. R. Acad. Sci., Paris* **301** 367
Schaefer D 1985 *The Physics of Finely Divided Matter* (Berlin: Springer)
Stephen M J 1978 *Phys. Rev. B* **17** 4444
Stockmayer W H 1976 *Molecular Fluids* (New York: Gordon and Breach)
Straley J P 1980 *J. Phys. C: Solid State Phys.* **13** 819
Vicsek T and Family F 1984 *Phys. Rev. Lett.* **52** 1669