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LETTER TO THE EDITOR

Distribution of relaxation times near the gelation threshold

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Abstract. We consider the distribution of relaxation times of randomly branched polymers in a sol, or of a gel in the reaction bath, close to the gelation threshold. We find that it is a slowly decaying power law with a cutoff at large times. This distribution cannot be characterised by one single time, but by two different times. Both diverge as one approaches the threshold, with different exponents depending on the percolation exponents s and t for the conductivity and the superconductivity respectively. These results also apply to mixtures of conductors and dielectric materials.

The viscoelastic properties of branched polymers and gels are of considerable practical importance, and have received a very large experimental and theoretical attention [1-4]. Our understanding of these fundamental properties in the vicinity of the gelation threshold, however, is rather limited. More specifically, we know that these systems are characterised by a large distribution of relaxation times and it is extremely interesting to have some information about such a distribution. Indeed the latter allows for the calculation of all macroscopic relaxation properties. Linear polymer melts are also known to have a large distribution of times, but it has been shown that these are related to a single time, namely the reptation time. We would like to know if in the case of branched polymers the distribution of times may also be reduced to a single time or if it is so large that it may not. As we will see, the latter is valid: in addition to a time proportional to the viscosity, a second, longer, characteristic time may be defined. The distribution of times is very large and may not be reduced to a single time. An important step was the recognition by de Gennes that the elastic modulus of the gel and the viscosity of the sol in the reaction bath are directly related to the conductance of a random resistor network [5] and a random superconducting network [6, 7] respectively. Thus the elastic modulus goes to zero as the threshold is approached from above as

$$G' \sim (p - p_c)^t \quad p > p_c \quad (1)$$

and the viscosity diverges as p_c is approached from below as

$$\eta' \sim (p_c - p)^{-s} \quad p < p_c \quad (2)$$

where s and t are the usual percolation superconductivity and conductivity exponents respectively, and $(p - p_c)$ the distance to the gelation threshold. It is very important to realise that both the above relations are the zero-frequency limits, above and below the threshold, of a complex modulus. For non-zero frequencies, this modulus $\bar{G}(\omega)$ has non-vanishing real and imaginary parts [8]. Conversely, one may also define a complex viscosity $\bar{\eta}$, directly related to the complex modulus:

$$\bar{G}(\omega) = G' + i\omega\bar{\eta} \equiv i\omega\bar{\eta}(\omega) \quad (3)$$

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with $i = \sqrt{-1}$ and ω the frequency. In the following, we will focus on the properties of the complex viscosity $\bar{\eta}(\omega)$. The latter was related [9, 10] to the complex dielectric constant $\bar{\epsilon}(\omega)$ of a random mixture of dielectric and metallic materials. Thus the present discussion applies also to the distribution of times near the percolation threshold of these mixtures. The scaling properties of $\bar{\epsilon}(\omega)$ were considered earlier by Efros and Shklovskii [11] and Clerc *et al* [12]. Thus we will assume [8] the following form for the viscosity:

$$\bar{\eta}(\omega) \sim (p - p_c)^{-s} f_{\pm}(i\omega(p - p_c)^{-s-t}) \quad (4)$$

with f_{\pm} an unknown scaling function with known limits both above (+) and below (-) the threshold for low and high frequencies [8]. Relation (4) displays a characteristic time T_z which diverges at the threshold:

$$T_z \sim (p - p_c)^{-s-t} \quad (5)$$

which may be interpreted as the longest relaxation time in the system[†].

Because the distribution of molecular weights is wide and may be characterised by two diverging masses, one wonders if such is not also the case for the distribution of times. Because we know the frequency dependence of the complex viscosity, it is possible to determine the distribution of relaxation times of a sol or a gel in the reaction bath. Let $H(\tau)$ be this distribution. Then, we have [1]

$$\bar{\eta}(\omega) = \int_{\tau_0}^{\infty} \frac{H(\tau) d\tau}{1 + i\omega\tau} \quad (6)$$

with τ_0 a microscopic time. Assuming for the relaxation times distribution a scaling form similar to the distribution for the masses

$$H(\tau) \sim \tau^{-x} g_{\pm}(\tau(p - p_c)^y) \quad (7)$$

with $g_{\pm}(x)$ a function defined above (+) and below (-) the threshold, the exponents x and y are determined, using relations (4) and (6). We find $x = t/(s+t)$ and $y = s+t$ (for $d = 3$, this leads to $x = 0.75$ and $y = 2.55$), and thus

$$H(\tau) \sim \tau^{-t/(s+t)} g_{\pm}(\tau(p - p_c)^{s+t}). \quad (7a)$$

Let us stress that this form is a direct consequence of relations (4) and (6) above. It is straightforward to evaluate the moments of this distribution. We find

$$T = \int_{\tau_0}^{\infty} H(\tau) d\tau \left(\int_{\tau_0}^{\infty} \frac{H(\tau)}{\tau} d\tau \right)^{-1} \sim (p - p_c)^{-s} \quad (8)$$

where the denominator is dominated by its lower bound and does not diverge,

$$T_z = \int_{\tau_0}^{\infty} \tau H(\tau) d\tau \left(\int_{\tau_0}^{\infty} H(\tau) d\tau \right)^{-1} \sim (p - p_c)^{-s-t} \quad (9)$$

and

$$T_n = \int_{\tau_0}^{\infty} \tau^{n+1} H(\tau) d\tau \left(\int_{\tau_0}^{\infty} \tau^n H(\tau) d\tau \right)^{-1} \sim (p - p_c)^{-s-t} \sim T_z \quad (n \geq 1). \quad (10)$$

[†] This is equivalent to the rotation time discussed earlier by Joanny [13] if we accept Straley's conjecture [14] that $s+t = \nu d$. The latter is correct in a Flory approximation.

Thus the distribution of times may not be reduced to a single time. There appear two diverging times: in addition to the time T_z that was considered earlier (see footnote† and also [15]), there is a shorter time, T , diverging at the threshold like the viscosity. The latter result is a direct consequence of relation (6) in the limit of zero frequency: below the threshold, the viscosity of the sol is [1]

$$\eta' = \bar{\eta}(\omega = 0) \quad p < p_c. \quad (11)$$

Note that in a *linear* polymer melt, because the modulus is finite, there is only one characteristic time, proportional to the viscosity.

It is tempting to relate the time distribution function and the molecular weight distribution. Let $P(N, p - p_c)$ be the number of polymers with N monomers per unit volume. We know that its scaling form [16]

$$P(N, p - p_c) \sim N^{-1-d/D} g\{(p - p_c)N^\sigma\} \quad (12)$$

where d is the dimension of space, and D is the fractal dimension [18] and σ is a percolation exponent [16, 19], exhibits a cutoff mass

$$N_z \sim (p - p_c)^{-1/\sigma}. \quad (13)$$

Comparing T_z , relation (9), to N_z , and generalising to all masses, we assume

$$\tau(N) \sim N^{(\bar{s} + \bar{t})/D} \quad (14)$$

where we have used known relations between percolation exponents, and $\bar{s} = s/\nu$ and $\bar{t} = t/\nu$ with ν the exponent of the connectivity length and D the fractal dimension [18]. Assuming

$$H(\tau) d\tau = P(N, p - p_c) W(N) dN \quad (15)$$

where $W(N)$ is a weight function and using relations (7a), (12), (14) and (15), we find

$$W(N) \sim N^{(d + \bar{s})/D} \quad (16)$$

favouring high molecular weights. Again this weighting may be interpreted if we come back to equations (6) and (11)

$$\eta' \sim \int_{\tau_0}^{\infty} H(\tau) d\tau. \quad (11a)$$

Inserting equations (7a) and (14) in the above equation, we find

$$\eta' \sim \int_{\tau_0}^{\infty} N^{\bar{s}/D} h\left(\frac{N}{N_z}\right) \frac{dN}{N} \quad (17)$$

where N_z is the second moment of $P(N, p - p_c)$ as usual [16, 19]. Assuming a self-similar behaviour, the first term in the integral above may be interpreted as the contribution of every molecular weight to the viscosity,

$$\bar{\eta}(N) \sim N^{\bar{s}/D}.$$

† Finally, Martin and Wilcoxon [17] also found two different times, different from those discussed above, in a silica system close to its gelation threshold. Silica, however, does not always exhibit percolation properties. Thus our considerations about the viscoelastic behaviour have to be somewhat amended in these systems.

Relation (17) may then be written as

$$\eta' \sim \int \tilde{\eta}(N) N^{-1+d/D} NP(N, p-p_c) dN \quad (18)$$

which may be written in the form

$$\eta' \sim \int [\eta'(N)] NP(N, p-p_c) dN \quad (18')$$

where

$$[\eta'(N)] \sim \eta'(N) N^{-1+d/D} \sim \eta'(N) \phi^{-1}(N) \quad (19)$$

may be interpreted as the intrinsic viscosity of mass N ($\phi(N)$ being the concentration in mass N). Thus the weight $W(N)$ is directly related to the composition law for the viscosity. We find that the viscosity of the reaction bath is the weight average of the intrinsic viscosities of the components, a result already discussed by Marrinan and Hermans [20] and Sievers [21].

As a conclusion we have shown that close to the gelation threshold there is a very large distribution of relaxation times, decaying as a power law and cut off at very large times. Such a distribution may not be reduced to a single time, as for linear chains in a melt. It is characterised by two different diverging times respectively proportional to the viscosity and to the ratio of the viscosity and the elastic modulus. Because of this slow decay, we expect singular relaxation behaviours. As an example, we may consider for instance the deformation at constant rate of strain $\dot{\gamma}$. Above the threshold, the variation with time x of the stress $\sigma(x)$ is

$$\sigma(x) \sim (p-p_c)^t \dot{\gamma} x + \dot{\gamma} \int_{-\infty}^{\infty} \tau H(\tau) (1 - e^{-x/\tau}) d \ln \tau. \quad (20)$$

Using relation (7a) for $H(\tau)$, we find

$$\sigma(x) \sim (p-p_c)^t \dot{\gamma} x + \dot{\gamma} x^{t/(s+t)} F(x(p-p_c)^{s+t}) \quad (20a)$$

where the function $F(x)$ may be calculated using relation (20) when we know the distribution $H(\tau)$. A more detailed discussion of these relaxation effects will be given elsewhere. Trying to relate the distributions of molecular weights and of times leads to the law of composition of viscosities: we find that the viscosity of the bath is the weight average of the intrinsic viscosities of every mass.

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