

Exponent of 10/3 for the relaxation time of polymer chains

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A new model predicts a behavior $\tau \sim N^{10/3} N_e^{-4/3} [1 - (N_e/N)^{1/2}]^{2/3}$ for the maximum relaxation time for a melt of polymer chains of N monomers (with an average of N_e monomers per entanglement). This prediction agrees with the experimental result $\tau \sim (N/N_e)^{3.4} N_e^2$.

Models based on the concept of reptation¹⁻⁵ for a melt of polymer chains consisting of N monomers, with an average of N_e monomers between successive entanglements along one chain, correctly predict the behavior $D \sim N_e/N^2$ for the translational diffusion coefficient and the relation $\tau \sim \eta$ for the viscosity η and the maximum relaxation time. However, the prediction $\tau \sim N^3$ {along with the correction $\tau \sim N^3 N_e^{-1} (1 - \mu) N_e/N)^{1/2}$ }, where $\mu \geq 1.47$ for a continuous Routh chain^{4,5} (μ is actually used as an adjustable parameter)}, apparently does not explain the experimentally established behavior⁶⁻⁹ $\eta \sim \tau \sim N^{3.4}$. There is a corresponding discrepancy between theory and experiment for the maximum relaxation time of chains in a network. There is a brief but comprehensive discussion of the present state of the problem, including the most recent studies, in Ref. 10.

I share the opinion^{10,11} that the failure of the prediction is a consequence of the single-chain approximation. It is not at all obvious that the time over which a chain creeps within a tube (in reptation theory), i.e., the tube renewal time (which could be calculated in a different way, without leaning on the concept of reptation), is the same as the maximum relaxation time. The chain remains entangled with the same (spatially closest) chains (with the same region of the network in the case of chains in a network), but in a different way.

Weiss *et al.*¹¹ have offered the estimate $\tau \sim N^{10/3} / (\ln N)^{2/3}$ as the time of the first creep of $\sim N^{1/2}$ chains outside a sphere of radius $\sim N^{1/2}$ for a melt. A chain inside a sphere of radius $\sim N^{1/2}$ has $\sim R^3/N \sim N^{1/2}$ "neighboring" chains. Despite the successful prediction of an exponent of 10/3 for a melt, however, the specific physical suggestion of Ref. 11 looks a bit eccentric after a renormalization in accordance with $\tau \sim N^{10/3} N_e^{-4/3} / [\ln(N/N_e)]^{2/3}$. It is difficult to agree with the hypothesis that the behavior of an ensemble of $\sim (N/N_e)^{1/2}$ chains, i.e., the autocorrelation function of degree $\sim (N/N_e)^{1/2}$, would make the governing contribution to the dependence of τ on N . Furthermore, the discussion of Ref. 11 cannot be extended to the case of chains inside a network. The agreement of the exponents of 3.4 found experimentally in the two cases is a consequence of a common physical mechanism. The relation $\tau_{\text{relax}}/\tau_{\text{diff}} \sim N^{1/3}$, where τ_{relax} is the relaxation time of the tube, i.e., the time for a total loss of memory about the chain which was in the tube at zero time, and τ_{diff} is the time required for the traversal by diffusion of a distance on the order of the inertial radius

of the chain, was derived in Ref. 10. If we assume $\tau \sim \tau_{\text{relax}}$, we find $\tau \sim N^{10/3}$ (or $\sim N^{10/3} N_e^{-4/3}$). A development of the technique of Ref. 10 can apparently make it possible to also derive a correction factor which gives the rate of convergence on an exponent of 10/3, for comparison with that found in the present study.

In the present study we estimate the maximum relaxation time of the melt in a different way: as the time over which one chain "spreads out," as the result of translational diffusion, over a spatial region of size L such that the chain is, on the average, topologically decoupled from its original "partners," i.e., from the chains which were spatial neighbors. We can estimate the decoupling time for two Gaussian chains of N monomers. We assume the length of a monomer to be l , and we assume that both chains are inside a sphere of radius L . We estimate the degree of entanglement: We paste a film of minimum area on the first chain. The area of the film is then $\sim Nl^2$. The degree of entanglement is proportional to the number of intersections of the second chain with the film, i.e., $\sim N^2/(L/l)^3$, because of the ability of the chains to form knots. If the second chain intersects the film n times, then the probability that the chains are not entangled falls off no more slowly than exponentially with n ($n \ll N$), although the mathematical expectation of the absolute value of the Gauss invariant of the entanglement is $\sim \sqrt{n}$.

If $L/l \sim N^{1/2}$, then the probability for nonentanglement of two annular chains of N monomers is correspondingly estimated to be $\exp(-\beta N^{1/2})$. In connection with this result, we refer the reader to Eq. (18) of Ref. 12 and the derivation of that equation. Let us compare the results with the results of numerical simulations,^{13,14} in which a dependence $P_0 = 1 - A_0 \exp(-\alpha_0 R^3)$ is proposed for the probability for the nonentanglement of two annular chains whose centers of mass are separated by a distance R . The quantity A_0 tends toward one with increasing N , and we have $\alpha_0 \sim N^{-1.7}$. If we take an average of P_0 over the interior of a sphere of radius $\sim N^{1/2}$, we find the quantity $(1 - A_0)$, which takes on the values^{13,14} 0.34, 0.25, 0.18, and 0.13 for chains of lengths 20, 40, 60, and 80, respectively. The correspondence is satisfactory.

A more accurate estimate follows from the known analogy¹⁵ with the motion of a charged particle in a magnetic field. We denote by \mathbf{H} the magnetic field of a unit current flowing along the first chain. The energy of the field outside the chain is $\sim (N - N^{1/2})l$. An estimate follows from considerations of the renormalization-group type. Switching from N to gN , we find the equation

$$g(N + xN^y)l + (g + xg^y)N^{1/2}l = [gN + (xgN)^y]l \quad (1)$$

and thus $x = -1$ and $y = 1/2$.

Correspondingly, the degree of entanglement is $\sim N^2(1 - N^{-1/2})/(L/l)^3$. If this degree of entanglement is to be ~ 1 , i.e., if the chains are to be decoupled on the average, we must have $L \sim N^{2/3}(1 - N^{-2/3})^{1/3}l$. This situation would require a time $\tau_2 \sim L^2/D \sim N^{10/3}(1 - N^{-1/2})^{2/3}$.

We find an identical estimate for the time τ_k ($k \geq 3$) for decoupling, in the sense used above, of a chain with $(k-1)$ partners. It is reasonable to suggest that the

maximum relaxation time satisfies $\tau \sim \tau_2 \sim \tau_k$, where k is bounded. Taking N_e into account, we then find

$$\tau \sim N^{10/3} N_e^{-4/3} [1 - (N_e/N)^{1/2}]^{2/3}. \quad (2)$$

For a chain in a network with a sparse cross-linking (e.g., the number of monomers between linkages is $\sim N$), this discussion is modified in the following way: The "intersection" of a chain with its own trajectory at zero time is estimated to be $\sim N^2/(L/l)^3 \sim 1$; using N_e , we find $\tau_0 \sim N^{10/3} N_e^{-4/3}$.

The arguments above support the hypothesis that as $N \rightarrow \infty$, the relaxation time has an asymptotic behavior $\tau \sim N^{10/3}$.

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