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Dynamics of Entangled Flexible Polymers

Monte Carlo Simulations and their Interpretation

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Monte Carlo simulations have been reviewed for several models of dense polymer systems: (i) a system of very short ($N = 16$ links) freely joined chains with Lennard-Jones interactions in the continuum, (ii) self-avoiding walks on a diamond lattice with up to $N = 200$ links and (iii) pearl-necklace chains with up to $N = 98$ hard spheres. The cases of both a mobile and a frozen-in environment have been considered. The dynamics of displacements and the structure factors have been studied and interpreted in terms of the Rouse model and the reptation model, paying particular attention to the crossover between these models. Only for the frozen-environment case is reptation fully verified, while for models (i) and (ii) simple Rouse behaviour is found and for model (iii) relaxation with a diffusion constant $D \propto N^{-2.0 \pm 0.2}$ and disengagement time $\tau_d \propto N^{3.4 \pm 0.4}$ is found, but the monomer displacements are in disagreement with reptation laws. A brief comparison with pertinent experiments has been made, and the crossover between the Rouse model and the Zimm model is considered briefly.

1. INTRODUCTION

CURRENT MODELS FOR CHAIN DYNAMICS

Static properties of long, flexible polymers in dilute and semi-dilute solutions are understood by renormalization group methods,¹ and in concentrated solutions or melts they follow trivial random-walk statistics (radius $R \approx lN^{1/2}$ for chains of N links of length l).² Dynamic properties, in contrast, are less well understood, and current theoretical discussions rest on very simplified models.³⁻¹⁹ In the Rouse model,^{3,7} the forces of the environment on a chain are represented by a heat bath inducing local conformational changes. The characteristic time τ_q over which fluctuations characterized by a wavevector q decay is then^{3,7,9}

$$\tau_q^{-1} \approx \begin{cases} W(lq)^{2+1/\nu}, & qR > 1, \quad R \approx lN^\nu \\ Dq^2, & qR < 1, \quad D \approx l^2 W/N \end{cases} \quad (1a)$$

$$(1b)$$

where W is the rate at which links change their orientation and $\nu \approx 0.59$ for chains which are swollen due to excluded-volume interactions.¹ Eqn (1a) describes the relaxation for times t shorter than the chain-relaxation time, $\tau_{1/R} \propto W^{-1}N^{2\nu+1}$, while for $t > \tau_{1/R}$ diffusive behaviour, eqn (1b), dominates the motion for $qR > 1$.²⁰ Similarly, the monomer displacements $\langle r_i^2(t) \rangle$ behave as³

$$g(t) \equiv \langle r_i^2(t) \rangle \approx \begin{cases} l^2(Wt)^{1/2}, & t < \tau_{1/R} \\ Dt, & t > \tau_{1/R} \end{cases} \quad (2a)$$

$$(2b)$$

In the Zimm model,^{4, 8} the hydrodynamic backflow forces are also included. This is important for dilute solutions, where $W \propto \eta_0^{-1}$, η_0 being the solvent viscosity, and leads to

$$\tau_q^{-1} \approx \begin{cases} W(lq)^3, & qR > 1, \quad t < \tau_{1/R} \propto W^{-1} N^{3\nu} \\ Dq^2, & qR < 1 \text{ or } t > \tau_{1/R}. \end{cases} \quad (3a)$$

Instead of eqn (2a) for the monomer displacements, we now have $\langle r_i^2(t) \rangle \approx l^2(Wt)^{\frac{3}{2}}$ for $t < \tau_{1/R}$. These displacements show up in the 'incoherent scattering factor'

$$S_{\text{inc}}(q, t) \propto (1/N) \sum \langle \exp \{ i\mathbf{q} \cdot [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \} \rangle \approx \exp \left[-\frac{1}{6} q^2 \langle r_i^2(t) \rangle \right].$$

For both the Rouse and the Zimm model the coherent structure factor

$$S_{\text{coh}}(q, t) \propto N^{-2} \sum_{ij} \langle \exp \{ i\mathbf{q} \cdot [\mathbf{r}_i(t) - \mathbf{r}_j(0)] \} \rangle \quad (5a)$$

takes the simple form

$$S_{\text{coh}}(q, t) \propto \exp \left[-\text{const} (ql)^2 (Wt)^n \right], \quad Wt \gg 1 \quad (5b)$$

where the exponent $n = 1$ in the diffusive regime, while for $qR > 1$ and $t < \tau_{1/R}$ one has $n = \frac{1}{2}$ (Rouse model) or $n = \frac{2}{3}$ (Zimm model).

The 'reptation model' of de Gennes^{9, 12, 15} and Edwards^{10, 13} considers dense systems where the chains are entangled. It is thought that the effect of these entanglements is to create for each chain a tube of diameter d_T , such that the chains are restricted to snake-like motions along the tube axis. On the local scale inside the tube, *i.e.* for $\langle r_i^2(t) \rangle \lesssim d_T^2$, the chain performs Rouse-like motions [eqn (2)]. For larger times one has instead⁹

$$\langle r_i^2(t) \rangle \approx \begin{cases} ld_T(Wt)^{\frac{1}{2}}, & W^{-1}(d_T/l)^4 < t < \tau_{\text{Rouse}} \propto W^{-1} N^2 \\ ld_T(Wt/N)^{\frac{1}{2}}, & \tau_{\text{Rouse}} < t < \tau_d \propto (l/d_T)^2 N^3 \\ Dt, & t > \tau_d, \quad D \propto W d_T^2 N^{-2}. \end{cases} \quad (6a)$$

$$\langle r_i^2(t) \rangle \approx \begin{cases} ld_T(Wt/N)^{\frac{1}{2}}, & \tau_{\text{Rouse}} < t < \tau_d \propto (l/d_T)^2 N^3 \\ Dt, & t > \tau_d, \quad D \propto W d_T^2 N^{-2}. \end{cases} \quad (6b)$$

$$Dt, \quad t > \tau_d, \quad D \propto W d_T^2 N^{-2}. \quad (6c)$$

While this behaviour also shows up in $S_{\text{inc}}(q, t)$ [eqn (4)], $S_{\text{coh}}(q, t)$ is more complicated as there is no single time τ_q dominating the scattering under wavevector q .¹⁵ For $R^{-1} < q < d_T^{-1}$ it is predicted that $S_{\text{coh}}(q, t)$ decays non-exponentially towards a constant value¹⁵

$$S_{\text{coh}}(q, t)/S_{\text{coh}}(q, 0) \approx 1 - q^2 d_T^2/36, \quad t \ll \tau_d \quad (7a)$$

while later the relaxation should be independent of q

$$S_{\text{coh}}(q, t)/S_{\text{coh}}(q, 0) \approx \exp(-t/\tau_d), \quad t > \tau_d. \quad (7b)$$

All these models oversimplify the actual dynamics, which are those of a dense fluid in the local environment. It is not completely clear under which conditions these models are valid. In addition, one needs a better microscopic understanding of parameters such as W and d_T . In fact, while reptation seems to be a nice framework for bulk viscoelastic properties,¹³ the precise microscopic meaning of the entanglements is not so clear. We would also like to study the crossover between the various models which occurs when N or the concentration c of a polymer solution is varied.^{11, 12, 21} Even the derivation of some of the results is rather qualitative and doubts can be raised about their validity; *e.g.* it has been suggested²⁰ that instead of eqn (7b) one should have $S_{\text{coh}}(q, t)/S_{\text{coh}}(q, 0) \propto \exp(-Dq^2 t)$, for $t \gg \tau_d$, as in the case $qR < 1$.

Since Monte Carlo simulations have been useful for understanding static chain properties and the asymptotic laws valid for $N \rightarrow \infty$ could be verified for short chains,²² one expects simulations to be useful for chain dynamics also. Such

simulations have indeed been performed recently²³⁻²⁶ and have a bearing on the above models, as well as on neutron-scattering experiments.^{27, 28} In the following we have summarized these studies and pointed out some questions which still need answers.

2. SIMULATIONS OF SHORT CHAINS IN THE CONTINUUM

A simple model consists of rigid links of length l freely jointed together at arbitrary angles. Interactions can be introduced for example by postulating a Lennard-Jones potential $U(\mathbf{r}_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$ between any pairs of beads at points \mathbf{r}_i and \mathbf{r}_j [$\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$]. While ϵ determines the temperature scale, $\sigma \equiv 0.4l$ was chosen²³ since then the static properties follow asymptotic laws down to very small values of N .²⁹ Dynamics are introduced by randomly choosing a bead of chain i and moving it through a randomly chosen angle ϕ on a circle while keeping all other bead positions fixed. This trial move is accepted only if the transition probability $W(\mathbf{r}_i - \mathbf{r}_i')$ exceeds a random number η with $0 < \eta < 1$, otherwise it is rejected and another move is tried. A transition probability which both satisfies detailed balance with the equilibrium probability distribution, $P_0 \propto \exp(-\mathcal{H}/kT)$ where $\mathcal{H} = \sum U(\mathbf{r}_{ij})$ is the Hamiltonian of the system, and simulates entanglement restrictions is [$\delta\mathcal{H} \equiv \mathcal{H}(\mathbf{r}_{j \neq i}, \mathbf{r}_i) - \mathcal{H}(\mathbf{r}_{j \neq i}, \mathbf{r}_i')$]

$$W(\mathbf{r}_i \rightarrow \mathbf{r}_i') = \begin{cases} \exp(\delta\mathcal{H}/kT), & \text{if } \delta\mathcal{H} < 0 \\ 1, & \text{if } \delta\mathcal{H} \geq 0 \end{cases} \left\{ \begin{array}{l} \text{no intersection} \\ \text{no intersection} \end{array} \right. \quad (8a)$$

$$\left\{ \begin{array}{l} \text{no intersection} \\ \text{no intersection} \end{array} \right. \quad (8b)$$

$$0, \text{ if the move would require link intersection.} \quad (8c)$$

In our simulation of melts, eqn (8c) reduces the rate of accepted moves to *ca.* one-fifth of what it would be with eqn (8a) or (8b) alone. In the related work of Bishop *et al.*²⁴ longer chains [but only eqn (8a) and (8b)] are used; otherwise their results are similar to those of ref. (23).

As a first step, this model was studied in the dilute limit of isolated single chains with $N = 16$ links. It was found that eqn (1), (2), (4) and (5) account for the data. Only for very large q ($ql \gg 1$) does the gaussian approximation for $\mathbf{r}_i(t) - \mathbf{r}_i(0)$ involved in eqn (4) become invalid, as expected.

As a second step, 10 such chains were put in a box of size $L = 4l$, and periodic boundary conditions were applied to simulate a macroscopic system. Again the results are in agreement with the Rouse model, *cf.* fig. 1. Displacements $\langle r_i^2(t) \rangle$ and $S_{\text{inc}}(\mathbf{q}, t)$ show distinct the Rouse behaviour [eqn (2a)]. No intermediate reptation regime [eqn (6a)] is seen. Also $S_{\text{coh}}(\mathbf{q}, t)$ is in quantitative accord with Rouse behaviour. At longer times one sees crossover to diffusion of the chains as a whole. (Note the difference between S_{coh} in the laboratory system and in the centre-of-gravity system in fig. 1; the crossover occurs at $t \approx \tau_{1/R}$ independent of q , in accord with theory.²⁰)

As a third step, after equilibrating this system the configurations of all but one of the chains were frozen-in and only one chain allowed to move. Thus we simulated the situation of one chain moving in the presence of randomly fixed obstacles.⁹ Now the predicted behaviour $\langle r_i^2(t) \rangle \propto t^{1/2}$ [eqn (6a)] was readily seen over at least three decades of time, and in the same time interval the centre of gravity \mathbf{r}_{cg} followed the law⁹ $\langle r_{\text{cg}}^2(t) \rangle \propto t^{1/2}$. These results prove that in spite of the shortness of the chains there must be many entanglements along each chain. Furthermore, the geometry of these entanglements at the time when we stop the movements of all other chains does not change substantially. Hence the fact that in the frozen-in case we clearly see reptation and in the mobile case we do not show that d_T should not be linked exclusively to

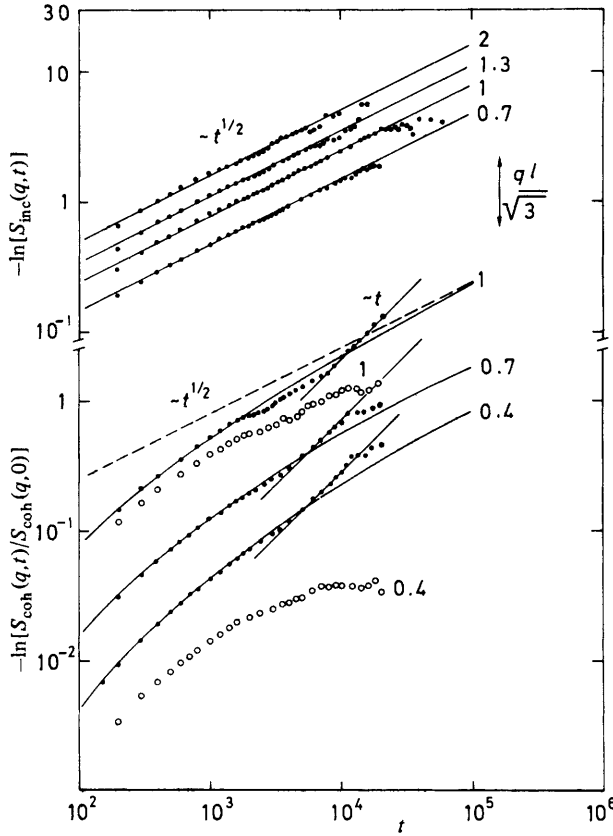


Fig. 1. Log-log plot of $S_{\text{inc}}(q, t)$ (upper part) and $S_{\text{coh}}(q, t)/S_{\text{coh}}(q, 0)$ (lower part) against time (in units of attempted moves per bead) for various q . Solid curves represent the Rouse model prediction where the rate W [eqn (1)] was adjusted ($W \approx 0.025$ in our time units). Open circles represent the structure factor in a coordinate system in which the centre of gravity of the considered chain would be at rest. $c = 2.5$, $kT/\epsilon = 3$. From ref. (23).

geometrical constraints of chain configurations, but should also take into account the local chain mobility.

Of course, one may quote many reasons why melt simulations fail to see reptation: (i) chain lengths N too short, (ii) chain density too low, (iii) temperature too high or (iv) reptation model inadequate. In order to check for (ii) and (iii), simulations were also performed at a four times higher density and at $kT/\epsilon = 0.4$, respectively. In both cases the chains were found to be frozen into a sort of glass-like state, with displacements $\langle r_i^2(t) \rangle \leq 10^{-2} l^2$ over the timescales of interest.

3. SIMULATIONS OF LONG LATTICE CHAINS

Self-avoiding walks (SAW) on the diamond lattice with up to $N = 200$ steps were simulated²⁵ at a concentration of $c \approx 0.344$. The analysis of static properties revealed that on a small scale (within blobs of size $N_B \approx 20$) the chains are still 'swollen', while on a larger scale the chains behave like ideal random walks. However, simple Rouse

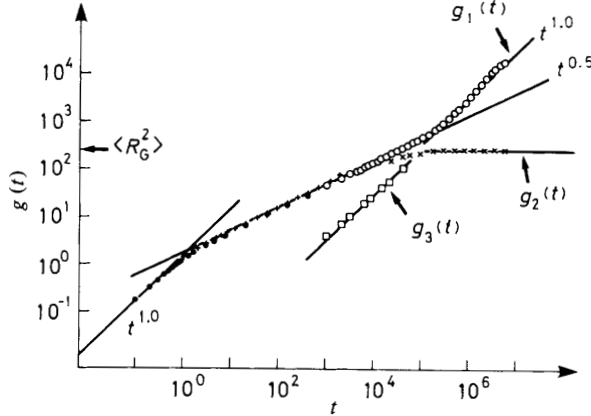


Fig. 2. Log-log plot of $g_1(t) = (1/20) \sum_{i=0}^{10} \langle r_i^2(t) \rangle$ against time, the latter measured in attempted moves per bond, for chains with $N = 200$ at the tetrahedral lattice and a concentration $c = 0.344$. $g_2(t)$ is the same mean-square displacement of inner monomers of the chain measured in the centre-of-gravity systems of each chain, while $g_3(t) \equiv \langle r_{cg}^2(t) \rangle$. From ref. (25).

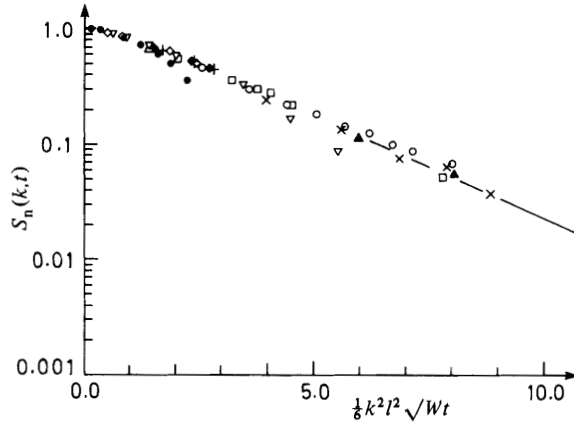


Fig. 3. Coherent structure factor $S_{coh}(q, t)/S_{coh}(q, 0)$ for a system of chains with 200 links moving on a tetrahedral lattice at a concentration $c = 0.344$. Data are plotted in semilog form against the variable $(1/6)q^2 l^2 \sqrt{Wt}$ to verify the asymptotic decay proportional to $\exp(-\text{const } q^2 l^2 \sqrt{Wt})$ predicted by the Rouse model. The parameter W is set equal to unity. $k = \bullet, 0.1$; $\nabla, 0.2$; $+, 0.25$; $\square, 0.3$; $\circ, 0.4$; $\times, 0.5$; $\blacktriangle, 0.6$. Experimental data (\diamond) for poly(dimethyl siloxane) melts²⁷ and the simulation data of fig. 1 (\blacklozenge) are also included, fitting $W = 4.3$ for both. From ref. (25).

behaviour is again observed even for the longest chains (fig. 2). It is seen that eqn (2a) holds until the mean-square displacement becomes of the order of the square of the gyration radius $\langle R_G^2 \rangle$ of the chain; then diffusion of the chain as a whole takes over.

Also, $S_{coh}(q, t)$ (fig. 3) confirms the Rouse-like behaviour. The simulation shows that in the regime where one probes the internal motions of the chains the normalized structure factor depends on q and t as $q^2 \sqrt{t}$ only. Deviations from this behaviour, which lead to quicker decay, are seen at long times and are due to the diffusive motion of the chains. By contrast, according to the reptation model one would expect a

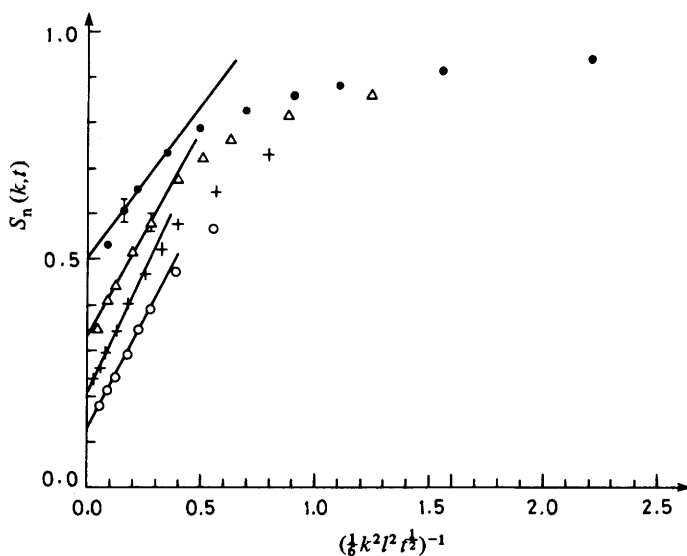


Fig. 4. Coherent structure factor $S_{\text{coh}}(\mathbf{q}, t)/S_{\text{coh}}(\mathbf{q}, 0)$ plotted against $(\frac{1}{6} q^2 l^2 \sqrt{Wt})^{-1}$ for the case of a single mobile chain in a frozen-in environment. Intercepts are used to estimate the tube diameter d_T from eqn (7a). From ref. (25).

	k	$S(k, t = \infty)$	d_T	N_e
●	0.3	0.50 ± 0.05	275	45 ± 10
△	0.4	0.33 ± 0.05	250	41 ± 5
+	0.5	0.21 ± 0.02	225	38 ± 5
○	0.6	0.13 ± 0.02	205	34 ± 5

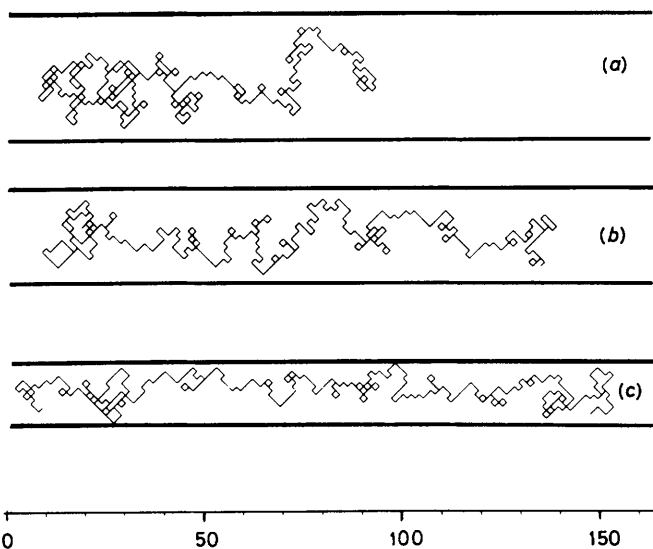


Fig. 5. Planar projections of 'snapshots' of chain configurations on the tetrahedral lattice confined to straight tubes of various diameters d_T : (a) 32, (b) 24 and (c) 16 ($N = 400$, $l = \sqrt{3}$). From ref. (31).

crossover to slower decay, and the data should not scale as there is an additional dependence on the parameter qd_T .²⁷ Such behaviour occurs if the environment of the moving chain is frozen-in (fig. 4). The resulting tube diameter $d_T \approx 10$ lattice spacings is of the same order as the length over which the SAW interaction is screened out, in rough agreement with the expectation¹² that there should be only one characteristic length in the system. Obviously this is not true in melts: the screening length is of the order of a few Å (monomer distances). Estimates for d_T extracted from viscoelastic properties^{13, 30} are $d_T \approx 30\text{--}80$ Å. If d_T were so large for real systems, the experimental data²⁷ included in fig. 3 would satisfy $qd_T \gtrsim 2$ and might then be affected only weakly by the tube constraints. Thus it is necessary to study in more detail the crossover from Rouse to reptation behaviour. As a first step, simulations of chains in straight tubes of various diameters have begun (fig. 5).³¹

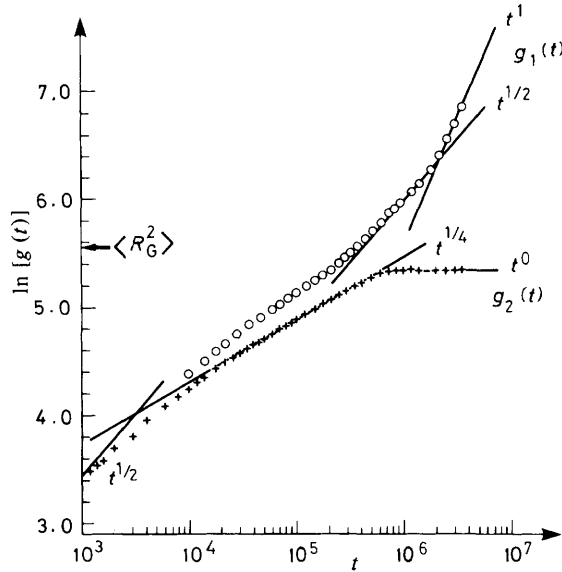


Fig. 6. Log-log plot of $g_1(t)$ against time for the single mobile chain ($N = 200$) in a frozen-in environment built up by similar chains at $c = 0.344$. $g_2(t)$ is the mean-square displacement measured in the centre-of-gravity system. From ref. (25).

While there are still uncertainties about coherent scattering from one reptating chain,^{15, 20, 23, 25} the predictions⁹ [eqn (6a) and (6b)] for the displacements are verified when one considers a chain in a frozen-in environment (fig. 6): Rouse behaviour occurs for $\langle r_i^2(t) \rangle \lesssim d_T^2$, while $\langle r_i^2(t) \rangle \propto t^{1/2}$ holds until $\langle r_i^2(t) \rangle$ reaches $\langle R_G^2 \rangle$, where one again finds $\langle r_i^2(t) \rangle \propto t^{1/2}$ until at τ_d diffusive behaviour sets in [eqn (6c)]. Estimates for d_T extracted from the various regimes are consistent with each other.²⁵

One may again suspect, of course, that the failure to see reptation in the case where all chains are mobile might be due to too short chains and/or too small concentration.³² This is not the case for the experimental data in fig. 3: the molecular weight used ($M_w = 60000$) is safely in the regime where the viscosity behaves as $\eta \propto M_w^{3.4}$ (this regime starts at $M_w \approx 15000$ ²⁷), and hence the chains are long enough to be in the strongly entangled regime.

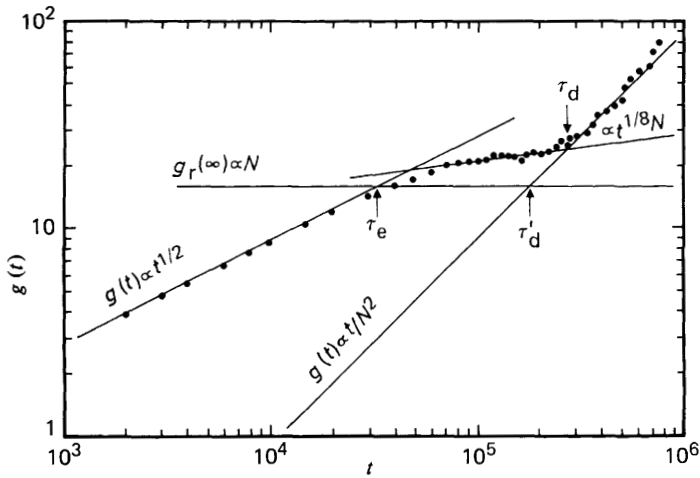


Fig. 7. Log-log plot of $g(t)$ against time for a system of 24 chains of 'pearl-necklace' chains with $N = 72$ hard spheres each. Intersections of the straight lines serve to define various crossover times τ_e , τ'_d and τ_d . From ref. (26).

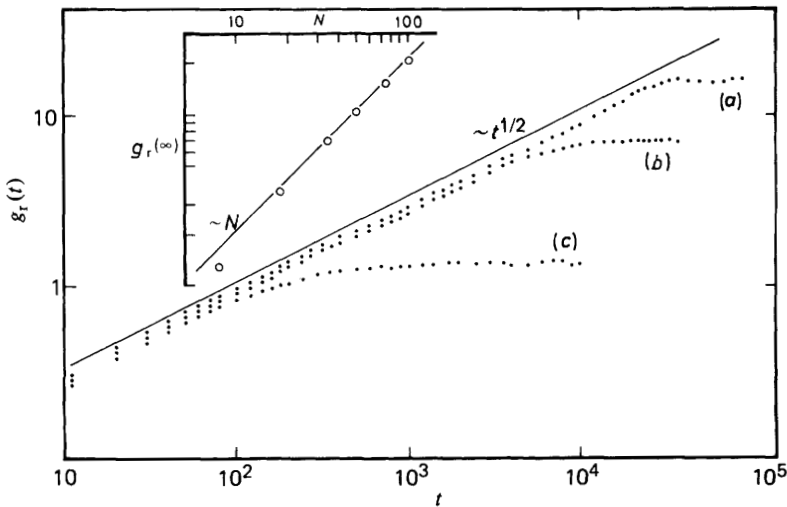


Fig. 8. Log-log plot of the mean-square displacement in the centre-of-gravity system plotted against time for several N : (a) 72, (b) 32 and (c) 18. The chain-length dependence of the asymptotic value $g_r^{(\infty)}$ is plotted in the upper left-hand corner. From ref. (26).

4. SIMULATIONS OF LONG CHAINS IN THE CONTINUUM

The most extensive simulations to date²⁶ concern ensembles of N_p chains, each consisting of N hard spheres of diameter $h/l = 0.9$ freely joined together, put in a box of size L chosen such that the concentration $c = N_p N / (L/l)^3 = 0.7$, for N up to 98 (and N_p up to 28). In this case the diffusion constant for $N \gtrsim 40$ is indeed consistent with the reptation law [eqn (6c)] $D \propto N^{-2}$, as also found experimentally.³³ However, the mean-square displacements do not follow the reptation predictions (fig. 7 and 8):

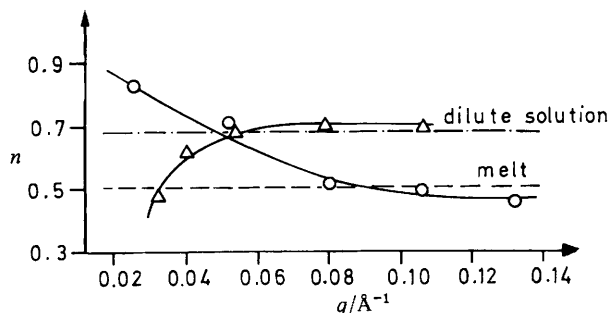


Fig. 9. Exponent n [defined in eqn (5b)] plotted against wavevector q for poly(dimethyl siloxane) dissolved in deuterated benzene at concentrations $c = 0.18$ (triangles) and $c = 0.45$ (circles). From ref. (28).

both $g(t)$ and the squared displacement in the centre-of-gravity system $g_r(t)$ increase proportionally to $t^{\frac{1}{2}}$ until $t \approx \tau_{\text{Rouse}}$, where $g_r(t)$ saturates at $g_r(\infty) \propto N$. Note the contrast between $g_r(t)$ in fig. 8 and $g_2(t)$ in fig. 6: $g_r(t)$ does not show dependence on $t^{\frac{1}{2}}$, in contrast with the case of the frozen-in environment. Since the saturation value satisfies $g_r(\infty) \propto N$, the time τ_e where crossover to this value occurs must be identified as the relaxation time $\tau_{\text{Rouse}} \propto W^{-1}N^2$. However, while in fig. 2 diffusion sets in at this time [and therefore $D \propto 1/N$ since $D\tau_{\text{Rouse}} \approx g_r(\infty) \propto N$], in fig. 7 the displacements increase more slowly after this time and diffusion sets in at a much later time τ_d , which varies with chain length as²⁶ $\tau_d \propto N^{3.4 \pm 0.4}$.

If this displacement behaviour in polymer melts persists for $N \rightarrow \infty$, it implies that reptation theory^{9, 15} cannot apply. At present it cannot yet be excluded that the behaviour seen in fig. 7 and 8 is particular to the regime for crossover from Rouse to reptative behaviour. If so, fig. 4 and 6–8 imply that this crossover behaviour in melts is different from the crossover in the case of the frozen-in environment. Standard theory^{9, 15} does not distinguish between these two cases. However, various additional relaxation mechanisms might be important even if a tube model applies to melts: the tube may locally expand or contract²³ or the tube itself may show local Rouse-like diffusive motion together with the chain it contains; the topological constraints would be left invariant^{10, 13} under both these types of motion. It is not obvious to us that these mechanisms can be completely absorbed in an increase in the effective tube diameter d_T .

5. CROSSOVER FROM ZIMM TO ROUSE BEHAVIOUR IN CONCENTRATED SOLUTIONS

The hydrodynamic interactions important for dilute solutions⁴ are not easily incorporated into Monte Carlo simulations. It is believed^{11, 12, 21} that hydrodynamic interactions are screened in semidilute and concentrated solutions, and the Rouse model should then be applicable over a wide range of molecular weights. Then the simulations discussed in sections 2–4 might be compared to such systems.

Experiments on poly(dimethyl siloxane) dissolved in deuterated benzene at various concentrations have been carried out with the neutron spin-echo method.²⁸ Analysing the scattering with eqn (5b) shows a crossover from (unscreened) Zimm relaxation ($n = \frac{2}{3}$) seen at large q to Rouse behaviour ($n = \frac{1}{2}$) at smaller q for low concentrations (fig. 9), as expected. But surprisingly at higher concentrations a second crossover is

detected from Rouse behaviour back to Zimm behaviour upon decreasing q . This phenomenon has been interpreted by incomplete screening of the hydrodynamic interaction.²⁸ The average hydrodynamic forces are then modelled as²⁸

$$\langle f(r) \rangle \propto [\eta_0^{-1} - \eta^{-1}(c)] \langle \exp[-r/\xi_h(c)]/r \rangle + \eta^{-1}(c) \langle 1/r \rangle \quad (10)$$

where η_0 is the pure solvent viscosity, $\eta(c)$ some effective solution viscosity and $\xi_h(c)$ the hydrodynamic screening length. While the first term on the right-hand side of eqn (10) is standard,¹² the last term is new. It leads to behaviour described by the Zimm model, eqn (3a), in a regime $R^{-1} < q < [\eta_0/\eta(c)] \xi_h^{-1}(c)$, but with a reduced rate [$W \propto \eta^{-1}(c)$], screened Zimm relaxation.²⁸ It is unclear how this hydrodynamic response over intermediate-length scales interferes with entanglement restrictions.

6. CONCLUSIONS

Both neutron-scattering experiments and simulations reveal that the simple Rouse model has a wide range of applicability in understanding the time dependences of displacements and scattering intensity, even in cases where entanglements affect the centre-of-gravity motion and/or viscous response of the polymer solution or melt. The crossover from Rouse behaviour to entangled behaviour in melts seems to be different from cases with a frozen-in environment; only in the latter case do simulations verify the reptation concepts. The need for more detailed theories for this crossover regime emerges, since this regime also seems to be relevant for experiments.

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