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Slow Spreading of Polymer Melts

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ABSTRACT: We discuss the precursor film profiles expected to be encountered during the spreading of large N polymer melts. We introduce a new control parameter: the ratio f of bulk to substrate monomer mobility. As a function of f, a variety of shapes are encountered. For $f \approx 1$, the "sliding" profile of Brochard and de Gennes is recovered. With increasing f the macroscopic "foot" predicted by Brochard and de Gennes diminishes in height and eventually vanishes. For large f, the precursor is found to spread by a new mechanism: reptation instead of hydrodynamic flow. The new precursor profile is characterized by a shoulder or step with a height on the order of the radius of gyration of the polymers.

I. Introduction

The macroscopic properties of drops of low-viscosity fluids spreading over dry and smooth substrates are well understood.[1] The drop has the shape of a hemispherical cap whose radius increases with time and whose contact angle θ with the substrate decreases with time (Figure 1). The spreading velocity U of the drop is determined by a competition between the capillary pressure, favoring spreading, and viscous losses. This competition is expressed in Hoffman's law: $U \propto (\gamma/\eta)\theta^3$, with η the viscosity and γ the surface tension. Importantly, this spreading velocity is *not* dependent on the difference in surface energy of a wet and a dry surface. A measure of that difference is the spreading pressure S, defined by

$$S = \gamma_{sv} - \gamma_{sl} - \gamma \tag{1}$$

with γ_{sv} and γ_{sl} respectively the energy per unit area of the dry and the wet substrate. Of course, a positive value for S (wetting) is a necessary condition for spreading. For negative S (nonwetting), the contact angle is fixed by Young's law[2] $\gamma \cos(\theta) = \gamma_{sv} - \gamma_{sl}$.

It has been known since the days of Hardy that ahead of the macroscopic drop there exists a microscopically thin precursor film. This precursor film is due to the film-thickening "disjoining" pressure exerted by van der Waals forces between substrate and film. The driving force for the spreading is the combined effect of gradients in the capillary pressure and the disjoining pressure. The height profile $\zeta(x)$ of the precursor film was predicted, by Joanny and de Gennes[1,3] (JG), to be proportional to $1/x$, with x a coordinate along the substrate and perpendicular to the contact line (see Figure 1). The precursor film starts when the thickness of the droplet has fallen below a height a_0/θ, with $a_0 = (A/6\pi\gamma)^{1/2}$ a microscopic length (A is the Hamaker constant). Naively, we should have expected the drop to spread until its height has been reduced to that of a monolayer. JG predicted instead that due do the disjoining pressure, there should be a minimum height $e \approx a_0(\gamma/S)^{1/2}$, such that ζ cannot drop below e.

The spreading properties of drops of polymer melts are of particular intererest for technical applications (lubrification, paints, etc.). Because they are nonvolatile and because of their slow spreading velocities, large N polymer melts (with N the degree of polymerization) would be expected to provide us with a test case for the JG theory of precursor films. However, already the macroscopic spreading properties of polymer melt droplets offer unexpected features: the spreading velocity sometimes exceeds Hoffman's law[4] and deviations from the macroscopic drop shape have been noted.[5,6]

Recently, polarized reflection microscopy by Ausserre et al.[7] of drop profiles of large N (10^4–10^6) poly(dimethylsiloxane) (PDMS) melts, spreading over smooth silica surfaces, confirmed Hoffman's law. Detailed ellipsometry measurements by Leger et al.[8,9] showed that the drop thins out to a limiting thickness that is in fair agreement with the predicted value of e. They did find a precursor film, but the measured profile was in clear disagreement with the calculated profiles.[10]

Brochard and de Gennes[11] (BG) noted that we indeed should expect the precursor profiles of polymer melt droplets to be unusual. Because large N polymers are entangled with each other, polymer melts will resist shear flow. A precursor film spreading under a pressure gradient normally can only do so by shear flow because the flow velocity at the substrate is assumed zero. For large N melts, this is an unlikely scenario. One would rather expect[12] a thin melt film subjected to a pressure gradient to slip and slide over the substrate. If k is the friction coeffi-

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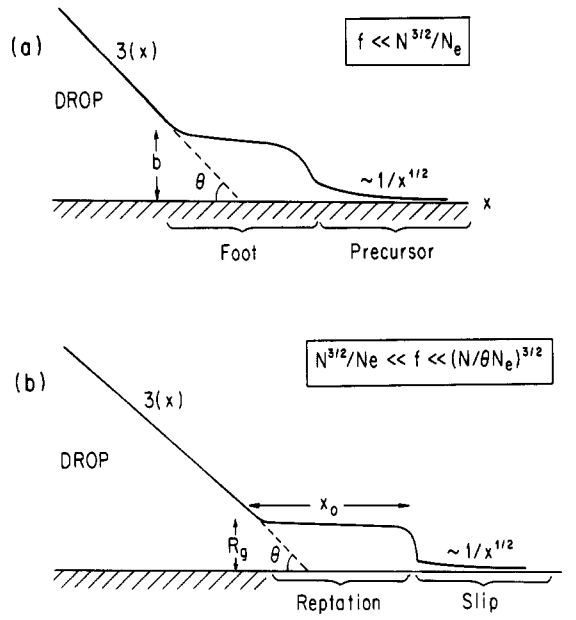

Figure 1. (a) Droplet profile for the case $f \ll N^{3/2}/N_e$. The precursor profile has a "foot" of height b. The height of the foot is reduced by a factor $1/f$ compared with the BG theory. (b) Droplet profile for the case $N^{3/2}/N_e \ll f \ll (N/\theta N_e)^{3/2}$. The "step" at the beginning of the precursor has a height on the order of R_g. Transport in the step is by reptation. Transport in the more remote part of the precursor is by slip.

cient of this slipping film, then the spreading velocity would be

$$kU = -\zeta(x)\, dP/dx \tag{2}$$

with P the pressure (and $\zeta(x)$ the film height). For small ζ, we can neglect the capillary pressure and identify P with the disjoining pressure for the nonretarded van der Waals interaction $\Pi = A/6\pi\zeta^3$. The solution of eq 2 is

$$\zeta(x) \approx (A/[kUx])^{1/2} \tag{3}$$

Note the different dependence on x compared to the JG theory. The precursor profile is of course time dependent; eq 3 is the profile in a frame moving with the spreading velocity.

The friction coefficient k of a melt with a smooth substrate should not depend on the length of the polymers because entanglement plays no role in the slippage. If there is no reduction in the monomer mobility near the surface (see section II), one expects k to be of order η_{mono}/a, with η_{mono} the viscosity of *individual* monomers (i.e., of a melt with $N = 1$) and a the monomer length.

BG predicted that in between the macroscopic drop and the precursor film, there should be a big "foot" in the profile (Figure 1a). This foot is required because the spreading drop must build up a pressure head to push the slipping precursor over the substrate. The foot should have a height b of order $(\eta/\eta_{mono})a$, with η the viscosity of the melt. For $N = 10^3$, this height is of order 10 μm and should easily be visible by ellipsometry. No such foot was seen by Leger et al. (and neither did the measured profile obey eq 3) although, as mentioned, other experiments had noted deviations from the hemispherical-cap shape.

In view of the discrepancies between different experiments and between experiment and theory, it is reasonable to assume that an important control parameter for polymer melt precursors has been overlooked. The basic premise of this paper is that the discrepancies must arise from differences in the substrates used in different experiments. In particular, reduction in mobility of polymers close to the substrate will be argued to be an essential effect in understanding polymer melt precursor films.

Assume a melt is flowing over a substrate. A polymer with some of its monomers in contact with the substrate ("attachment sites") could be severely slowed down if the substrate can trap monomers over shorter or longer times, for instance due to hydrogen bonding. There then would be little or no hydrodynamic flow in the melt in a layer with a thickness of the order of the radius of gyration R_g ("dead layer").

PDMS melts flowing between mica plates separated by a distance less than R_g indeed have been found to have a considerably enhanced viscosity,[13] providing evidence for the existence of a dead layer. In addition, the melt exerted a repulsive force on the plates with a range on the order of R_g.[14] We should not expect the macroscopic laws of fluid dynamics to remain valid for melts at distances less then R_g away from an attractive wall. We can think of R_g as the characteristic microscopic length scale of the problem. For large N, R_g is on the order of 100 Å, which is comparable to the height of a typical precursor film, and we need a different description for this "microscopic" range.

The aim of the paper is to compute the precursor profile of large N polymer melts for precursor film heights less then or comparable to R_g. In section II, we will formulate the "two-fluid" model and calculate the profile. In section III, we conclude with a discussion of the nonequilibrium effects that are expected to pose the most serious restrictions on the validity range of the proposed model.

II. Two-Fluid Model

For film heights $\zeta \gg R_g$, macroscopic hydrodynamics can be assumed to be valid. As ζ becomes comparable to R_g, more and more polymers will have one or more monomers in contact with the substrate and these polymers could be considerably slowed down, as argued in the introduction. A small remaining fraction of polymers will, however, have no attachments. They are still relatively mobile and can be expected to give an anomalously large contribution to the mass transport.

The transport mechanisms of these two separate species will be different. Polymers with attachments are mutually entangled and transport, if possible at all, presumably occurs by the slip mechanism of BG. The entangled polymers slide as a collective entity with relatively little shear. On the other hand, transport of the remaining polymers, with no attachments, cannot be by hydrodynamic flow. The attached polymers form a porous medium through which the mobile polymers must manage to sneak. We will assume the reptation model as the transport mechanism for mobile polymers. There are thus two very different possible modes of transport, which in the language of electrical circuits, are in paralel.

One may compare this situation with superfluid ^{4}He where mass transport is due to a combination of normal viscous flow and zero viscosity superflow. By analogy with ^{4}He, we will use a two-fluid model and write the flow velocity U as the sum of a reptation and a slippage contribution:

$$U = nU_r + (1-n)U_s \tag{4}$$

Here, n is the fraction of polymers with no attachments while U_r and U_s are respectively the flow velocities of the polymers without and with attachment sites, averaged over the height of the precursor. To determine U_r and U_s, we note that the mobile polymers are

reptating through a porous medium, sliding with velocity U_s under a pressure gradient. We will use Darcy's Law for transport in a porous medium in a frame moving with a velocity U_s

$$(U_r - U_s) = -K\, d\Pi/dx \tag{5}$$

with K the "permeability".

This permeability is on the order of $Na^3\mu/(1-n)$, with μ the polymer mobility in a bulk melt. This may be seen by noting that Na^3 is the volume per polymer, so Na^3 $d\Pi/dx$ is the average force per polymer. The average flow velocity $U_r - U_s$ is the product of the mobility and the average force. The factor $(1-n)^{-1}$ is included because the frictional force on the mobile chains should be proportional to the density $1-n$ of the porous medium; it is only valid for n small compared to one.

The mobility μ of a reptating polymer in a melt[15] is on the order of $\mu_{mono}N_e/N^2$ with μ_{mono} the monomer mobility and N_e the entanglement distance ($\approx$100). The resulting expression for the permeability is

$$K \approx (N_e/N)a^3\mu_{mono}/(1-n) \tag{6}$$

The force $\mathcal{F}_{rep} = n\, d\Pi/dx$ per unit volume on the mobile chains is, from eq 5

$$\mathcal{F}_{rep} = -nK^{-1}(U_r - U_s) \tag{7}$$

The entangled, slipping polymers feel two friction forces: a friction force due to the substrate, given by eq 2, and a friction force due to the mobile polymers, which by Newton's third law, is equal but opposite to $\mathcal{F}_{rep}$. If $\mathcal{F}_{slip}$ is the frictional force per unit volume on the slipping polymers, equal to $(1-n)\, d\Pi/dx$, then

$$\mathcal{F}_{slip} = -kU_s/\zeta - \mathcal{F}_{rep} \tag{8}$$

We can now solve eq 4, 7, and 8. Eliminating U_r and U_s gives

$$U = -(nK + (\zeta/k))\, d\Pi/dx \tag{9}$$

Returning to the analogy with electrical circuits, eq 9 states that for parallel transport we must add the "conductivities" nK and ζ/k to get the total conductivity.

To compute the fraction n of mobile polymers, we will use the assumption that the precursor is an ideal melt. Polymers in an equilibrium melt perform Gaussian random walks so in the bulk of the sample R_g is on the order of $aN^{1/2}$. If the spreading is sufficiently rapid, then the precursor film may not be an ideal melt as will be discussed later.

Assuming now that a polymer performs a Gaussian random walk, the polymer will touch the substrate roughly every $\mathcal{N}$ monomer distances, with $\zeta = a\mathcal{N}^{1/2}$. Let p be the probability that after $\mathcal{N}$ monomers the polymer has *not* touched the substrate. This probability will be some finite number independent of N. The probability $\mathcal{P}$ for a polymer not to touch the substrate after N monomers is then of order $p^{N/\mathcal{N}}$ *so* $\mathcal{P} \approx \exp[-(R_g/\zeta)^2|\ln(p)|]$. The fraction n of mobile polymers should be on the order of $\mathcal{P}$. Using the theory of random walks, it is possible to show that the actual answer is

$$n(\zeta) = (\text{const})(R_g/\zeta)\exp[-(R_g/\zeta)^2(\pi^2/8)] \tag{10}$$

if $\zeta \ll R_g$.

We now have in eq 9 a differntial equation for the profile. We will first consider the regime of small ζ.

(A) Slip Regime ($\zeta < \zeta_{co}$). For $\zeta \ll R_g$, $n(\zeta)$ is negligible and we can neglect the first term in eq 9. This reduces eq 9 to eq 2 so we are back in the slip regime of the BG theory. We must, however, assign a different value to the friction coefficient k. In the BG theory, k was related to the bulk monomer viscosity η_{mono} by $k \approx \eta_{mono}/a$ (or equivalently to the bulk monomer mobility μ_{mono} by $1/a^2\mu_{mono}$). The reduced mobility of polymers near the substrate will, however, produce an additional drag on the melt and thus an enhanced friction coefficient.

We will lump the substrate-specific effects into the dimensionless ratio $f = \mu_{mono}/\mu_s$ of the monomer mobilities in bulk (μ_{mono}) and on the surface (μ_s). Both mobilities are thermally activated and f could vary over many orders of magnitude. If the substrate does not impair the monomer mobility, then $f = 1$ and the BG theory should be valid. If, on the other hand, there is hydrogen bonding of the polymer to the substrate, then we expect $f \gg 1$. We will consider f as a phenomenological parameter whose value must be determined experimentally.

Replacing μ by μ_s in k gives the new estimate

$$k \approx f\eta_{mono}/a \tag{11}$$

This also means that the height of the foot is reduced:

$$b \approx f^{-1}(\eta/\eta_{mono})a \tag{12}$$

The profile $\zeta(x)$ still obeys eq 3 in this regime. It follows from eq 3 that ζ grows as we reduce x (i.e., approach the macroscopic drop). With increasing ζ, $n(\zeta)$ also grows. The two terms in eq 9 become comparable when ζ reaches a crossover height ζ_{co} such that $n(\zeta_{co})K = \zeta_{co}/K$ or

$$\zeta_{co} \approx R_g[\ln(fN_e/N^{3/2})]^{-1/2} \tag{13}$$

The validity range of the slip regime is then $\zeta < \zeta_{co}$. If f is small compared to $N^{3/2}/N_e$, then ζ_{co} exceeds R_g. Recall that the two-fluid model is only valid if ζ is less than R_g. Thus, if $f \ll N^{3/2}/N_e$, then we are *always* in the slip regime. For small values of f the BG theory is recovered. If $f \gg N^{3/2}/N_e$, then only the thin, remote part of the precursor obeys BG. There is no foot in this case because ζ_{co} acts as a cutoff.

(B) Reptation Regime ($R_g < \zeta < \zeta_{co}$). We now assume n to be small but finite. First write eq 9 in the form

$$U = -a^3(N_e/N)\mu_{mono}[n(\zeta) + (\zeta/a)(N/fN_e)] \times (A/2\pi\zeta^4)\, d\zeta/dx \tag{14}$$

by using eq 6 and 11 and the expression for the disjoining pressure. Because $n(\zeta)$ increases exponentially fast with ζ, we can neglect the second term practically immediately when $\zeta > \zeta_{co}$. The reptation term "shorts" the slip term. The differential equation for ζ, neglecting slip, is

$$U = -(\text{const})a^3A(N_e/N)\mu_{mono}(R_g/\zeta^5) \times \exp[-(R_g/\zeta)^2(\pi^2/8)]\, d\zeta/dx \tag{15}$$

which has the solution

$$((\pi^2/8)(R_g/\zeta)^2 + 1)\exp[-(\pi^2/8)(R_g/\zeta)^2] = -\gamma\left(\frac{NU}{N_e\mu_{mono}A}\right)(R_g/a)^3(x - x_0) \tag{16}$$

with γ a numerical constant. The integration constant x_0 is fixed by demanding that we join the precursor to the macroscopic drop at $x = 0$ with $\zeta(0) = R_g$ so

$$x_0 \approx \left(\frac{NU}{N_e\mu_{mono}A}\right)^{-1}(R_g/a)^{-3} \tag{17}$$

It follows from eq 16 that $\zeta(x)$ has a sharp step or shoulder at x_0 where it drops to zero. The reptation profile

eq 16 thus persists only over a finite distance x_0 away the macroscopic drop. Of course, the profile does not really fall to zero at x_0; once ζ drops below ζ_{co} the profile crosses over to the slip regime.

If we use Hoffman's law in eq 17 with $\eta = 1/a\mu$, then

$$x_0 \approx a(A/\gamma 2a^2)(N^{1/2}\theta^3)^{-1} \quad (18)$$

For $N = 10^4$ and $\theta = 0.1$, x_0 is on the order of 10 Å, which is neglible. As the droplet spreads and θ reduces to, say, $\theta = 0.01$, x_0 is on the order of 10^4 Å, which should be quite visible by ellipsometry. The two-fluid model is thus only relevant for small contact angles.

III. Nonequilibrium Effects

In the Introduction we mentioned that a polymer melt flowing between plates is known to exert a repulsive force on those plates with a range on the order of R_g. The reader could well ask why this force was not included, as it is larger then the van der Waals disjoining pressure. Such a force would seem to have an obvious explanation in terms of the entropy reduction of the polymers squeezed between the plates. However, ideal melts screen the effect of a boundary within a distance on the order of the monomer length[15] and such a repulsive force would have a range on the order of a monomer length. A repulsive force with a range of R_g *could* be present if the melt near the wall is not in equilibrium.[16] The condition for a flowing polymer melt to be in equilibrium is that the relaxation time τ exceeds the inverse shear rate $\dot{\gamma}^{-1}$. In particular, the results of the two-fluid model can only apply if $D = \dot{\gamma}\tau$ is small compared to one.

The parameter D is of course the Deborah number. For $D \gg 1$, other peculiar effects are expected as well. It is well-known[17] that for $D \gg 1$, the macroscopic flow behavior of polymer melts is very unusual (non-Newtonian flow). Non-Newtonian flow effects would deform the precursor profile. Furthermore, for large D the polymer coils could be severely elongated by shear flow, and this may reduce the number of attachment sites per polymer. We will compute the Deborah number at two places: in the macroscopic drop at the beginning of the precursor film and in the small ζ slip regime of the precursor.

At the beginning of the precursor, the film height is of order R_g so the shear rate $\dot{\gamma}$ is on the order of U/R_g. For τ we use the relaxation time of bulk melts[15] $\tau \approx \eta N_e a^3/k_b T$. Assuming Hoffman's law for U gives for D

$$D \approx (\gamma a^2/kT)(N_e/N^{1/2})\theta^3 \quad (19)$$

With γa^2 comparable to kT, the condition $D \ll 1$ will be satisfied as long as N^2 is large compares to N_e.

Next we compute D in the slip part of the precursor film. Both the relaxation time and the shear rate are different:

(i) The shear rate is *not* U/ζ, because the film is slipping (nearly) uniformly. We must compute the velocity difference between the top and the bottom of the precursor film and compare this with ζ. If $\sigma = \eta(dv/dz)$ is the stress in the precursor film near the substrate, then the flow velocity $v(0)$ at the substrate (roughly U) is $v(0) = k^{-1}\sigma$, by definition of the friction coefficient. The shear rate $\dot{\gamma} \approx dv/dz$ is then Uk/η or U/b (see eq 12).

(ii) The equilibration time $\tau(\zeta)$ of the film is of order $\tau(a/\zeta)f$ because if $\zeta \ll R_g$ then a fraction a/ζ of all monomers is in contact with the substrate and has its mobility reduced by f (assuming the polymer to be homogeneously distributed across the film). The Deborah number of the slipping film is then

$$D \approx U\tau a f/b\zeta \quad (20)$$

Using once more Hoffman's law for U, eq 12 for b, and $\eta = \eta_{mono}N^3/N_e^2$ gives

$$D(\zeta) \approx (\gamma a^2/kT)\theta^3(a/\zeta)f^2N_e^3/N^3 \quad (21)$$

The condition for the precursor film to be in equilibrium for small ζ is thus $f \ll (N/\theta N_e)^{3/2}$ (with $\zeta = a$). If this condition is not satisfied, then the thinner part of the precursor will be out of equilibrium. The crossover height ζ_{ne} below which the film is out of equilibrium is defined as $D(\zeta_{ne}) = 1$ or

$$\zeta_{ne} \approx a(\gamma a^2/kT)\theta^3 f^2 N_e^3/N^3 \quad (22)$$

We can now make a list of the different regimes as a function of the parameter f:

$f = \mu_{mono}/\mu_s$	spreading mechanism
$f \ll N^{3/2}/N_e$	slip regime
$N^{3/2}/N_e \ll f \ll (N/\theta N_e)^{3/2}$	reptation + slip
$f \gg (N/\theta N_e)^{3/2}$	non-Newtonian regime

It would be very interesting to give a satisfactory description of spreading in the nonequilibrium regime. Besides the effects already mentioned, we note that for large f and large D the top part of the precursor could spill over the bottom part. In that case, the polymers on the bottom could form a "coat" on top of the substrate. This may even restore the $\zeta \approx 1/x$ behavior. One may speculate that such a coat would have a thickness on the order of ζ_{ne}. However, because so many new phenomena are expected for $D \gg 1$, we will not attempt a quantitative description.

In summary, we have found that for the spreading of polymer melts on smooth substrates, there is a new control parameter, f, which is crucial for determining the precursor profile. The substrate thus affects the film profile not only through the spreading pressure S but also through the surface monomer mobility, which is proportional to f^{-1}. For large f, the profile consists of a reptation regime joined to a slip regime by a step. For small f, the BG slip profile holds throughout.

There appear to be no published values for f. The experiments of Leger et al. show that for PDMS on silica, f must exceed 10^4, otherwise they should have observed a foot. One could in principle measure f with fluorescent tracer techniques. The predicted reduction in surface monomer mobility of PDMS on silica by at least 4 orders of magnitude should be an easily visible effect. In addition, information on "non-Newtonian" precursors would be very interesting. The existence of a coat could also be investigated by tracer fluorescent techniques.

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Numerical Study of Hydrodynamic Radii of Polymer Chains in Θ Solvent

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ABSTRACT: We simulated polymer chains in Θ solvent by a random walk model and calculated the translational friction coefficients and the hydrodynamic radii of these chains by solving the hydrodynamic equations numerically. Thus the preaveraging approximation in the Kirkwood–Riseman theory is avoided. More than 25 polymer chains of size 900 segments were calculated. The average ratio $\langle R_h/R_g \rangle$ for long chains approaches 0.87 and the averaged $\langle R_h^{-1} \rangle^{-1}$ vs root-mean-square averaged R_g approaches 0.79; thus they agree well with the measurement.

The hydrodynamic behavior of polymer chains is an important subject in macromolecule science and has been studied extensively. By considering the hydrodynamic interactions between segments, Kirkwood and Riseman[1] have calculated the intrinsic viscosity and the translational diffusion coefficient of polymer chains. Their theory has shown that the scaling exponent β of the translational friction coefficient (and hence the hydrodynamic radius R_h) vs the molecular weight of polymer N ($R_h \sim N^\beta$) decreases from 1 to 0.5 describing the transition from free-draining to nondraining limit. Thus the ratio of the hydrodynamic radius vs the radius of gyration approaches a constant for large polymers. Efforts have been made to improve the original K–R theory by considering the flexibility of the chains and improving or avoiding the preaveraging approximation.[2-7] On the other hand, the rapid development in light scattering techniques has furnished highly accurate measurement of the translational friction coefficient,[8] and the result indicated that the Kirkwood–Riseman theory[1] and Zimm's theory[2] underestimated the ratio between the hydrodynamic radius and the radius of gyration. Zimm's Monte Carlo calculation has indicated that by avoiding the preaverage approximation the extrapolated value from numerical calculations did raise this ratio significantly.[9] Since Zimm's result is extrapolated from calculations that were limited to 50 segments, it is essential to extend the calculation to polymers of large sizes. In this paper we numerically solved the hydrodynamic interactions between chain segments and calculated the translation friction coefficient and the hydrodynamic radius. By directly solving the hydrodynamic equations, we avoided the preaveraging approximation used in the K–R theory and some other theories, and thus the fluctuations are considered. Our work is in the same line as Zimm's Monte Carlo study of the hydrodynamic property of polymer chains.[9] The major differences are that we used a different model to generate the configurations of the chains and we extended the calculation to larger chains of 900 segments as compared to 50 segments calculated by Zimm. The other difference is that we have used a modified Oseen tensor. As in Zimm's Monte Carlo calculation our model also neglected the flexibility of the chains and the internal friction proposed by Fixman.[10]

We generate random walks in a three-dimensional lattice, and the monomers are modeled by spherical beads at each lattice point where the walker passes. The walk is allowed to cross itself or to take an immediate back step, though only one bead is located on each crossing point. The diameter of the bead is chosen to be the lattice constant. This simple model retains the essential

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