

The influence of time-dependent hydrodynamics on polymer centre-of-mass motion

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Abstract. – We describe simulations of isolated ideal polymer chains consisting of N monomers. The solvent is simulated using a dissipative ideal gas maintained at a set temperature by a Lowe-Andersen thermostat. By choosing a particular ratio of the Kuhn length to the monomer hydrodynamic radius, long-polymer scaling of the diffusion coefficient holds even for chains composed of a few beads. However, this requires that the model capture the hydrodynamics correctly on length scales equivalent to a typical solvent particle separation. It does. The decay of the centre-of-mass velocity autocorrelation function, $C(t)$, for short chains scales rapidly to a function independent of N , so we can determine the long-polymer limit of the function. At long times it decays with an algebraic long-time tail of the form $C(t) \sim t^{-3/2}$. This is consistent with the predictions of theories that take into account the time dependence of the intra-polymer hydrodynamic interactions. We argue that the scaling of the decay implies that the intra-polymer hydrodynamic interactions propagate on a surprisingly rapid time scale.

Introduction. – Classic theories of polymer centre-of-mass motion [1] make the assumption that inertia is irrelevant. Hydrodynamic interactions between bits of the polymer are assumed to propagate instantaneously. In reality, this is not the case. In this letter we examine the effects of the finite propagation time on polymer centre-of-mass dynamics. To do so, we use a model for which time-dependent hydrodynamics is included by the use of an explicit simple model solvent.

Because polymers are very large molecules, their dynamics are slow. Thus, a computational approach which resolves atomistic detail is impractical. A long polymer must be drastically simplified (“renormalized”) so that it can be simulated on long time scales. However, we need to be able to argue that in some meaningful sense we capture the dynamics of the real polymer. There are practical difficulties in doing this. First, the dynamics of a polymer (in dilute solution) are largely determined by the hydrodynamic interactions between the monomers making up the solvent [1], so this effect must be included. Second, even if hydrodynamics

is included, the dynamics of a long polymer chain are not necessarily the same as those of a short one. Third, the time scales for the dynamic processes governing the behaviour of the polymer will similarly differ between short and long polymer systems. Within the context of the polymer velocity autocorrelation function, we address the first two and partially the third of the problems we outlined above. The idea of including an explicit model solvent has been applied elsewhere. Spenley [2] used dissipative particle dynamics to study short model excluded-volume chains and found reasonable agreement with theory in a parameter regime where the hydrodynamics is relatively unimportant. Malevanets and Yeomans [3] modelled the solvent using direct simulation Monte Carlo and found good agreement with theory for the centre-of-mass dynamics if they allowed for compressibility. The solvent was modelled using a lattice Boltzmann equation by Ahlrichs and Dünweg [4] who compared the dynamics of a chain of monomers interacting through a Lennard-Jones potential using both an explicit and model solvent. The results were in good agreement.

The system we consider is a single ideal chain. That is, the polymer is modelled as a set of connected particles with a root-mean-square separation between adjacent beads b (the Kuhn length). This model is a minimal representation of a real (flexible) polymer but predicts reasonably well the dynamic properties of dilute polymer solutions [5]. For our purposes here it is useful because renormalizing the static properties is straightforward, the full N -particle distribution function being known. Nonetheless, the dynamics of the model, with which we are concerned here, are not trivial. We will begin by considering the time scales involved and the hydrodynamics of polymer diffusion.

There are three time scales with which we need to concern ourselves. First, we have a sonic time τ_s (as with all particle model solvents, the solvent is compressible). This is the time it takes sound to travel a characteristic distance l , *i.e.* $\tau_s = l/c_s$, where c_s is the speed of sound. Second, we have a viscous time $\tau_\nu = l^2/\nu$, where ν is the kinematic viscosity of the solvent. This is the time it takes transverse momentum to diffuse a distance l . Finally, we have a diffusive time $\tau_D = l^2/D$, where D is the polymer diffusion coefficient. This is the time it takes a particle to diffuse a distance l . For a long polymer we have $\tau_s < \tau_\nu \ll \tau_D$. The diffusive time is the longest and this defines the “long” time scale. Although for a smaller polymer we can have $\tau_s \sim \tau_\nu$, it always remains true that the sonic and viscous times are very much less than the diffusive time and these define the “short” time scale. There is reason to think that the first condition $\tau_s < \tau_\nu$ is of lesser importance because, at least in a colloidal suspension, sound propagation plays a minor role [6]. Furthermore, it does not influence transport coefficients. This makes it surprising that Malevanets and Yeomans [3] had to allow for it.

Polymer dynamics. – The centre-of-mass diffusion coefficient, D , for a chain of N beads in a solvent with shear viscosity η at temperature T can be written as [7]

$$\frac{D}{D_0} = \frac{1}{N} + \frac{a}{N^2} \left\langle \sum_i \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right\rangle, \quad (1)$$

where D_0 is the diffusion coefficient a bead would have were it a single particle in the same solvent, and $a (= kT/(6\pi\eta D_0))$ defines a bead “hydrodynamic radius”. The first term represents the diffusion coefficient of N connected beads in the absence of hydrodynamic interactions (“Rouse” diffusion). The second is the collective hydrodynamic contribution due to the hydrodynamic interactions of particles with all their neighbours. For a long polymer ($N \rightarrow \infty$) this term is proportional to $1/\sqrt{N}$, so it dominates (Zimm scaling). It can be evaluated

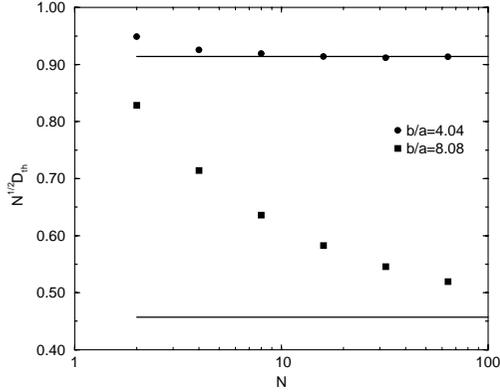


Fig. 1

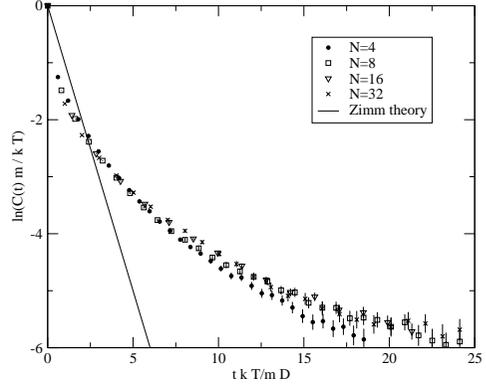


Fig. 2

Fig. 1 – Theoretical value for the polymer diffusion coefficient D_{th} as a function of the number of monomers N . The data correspond to the magic value of a/b (top) and twice the magic ratio (bottom). The solid lines are the corresponding asymptotic ($N \rightarrow \infty$) value.

Fig. 2 – The velocity correlation function $C(t)$ plotted in dimensionless form for chains composed of 2, 4, 8, 16 and 32 beads. The solid line is the prediction of Zimm theory.

analytically and yields

$$D = \left(\frac{8}{3} \sqrt{\frac{6}{\pi}} \right) \frac{kT}{6\pi\eta b\sqrt{N}}. \quad (2)$$

However, for finite N there are significant corrections to the asymptotic result (eq. (2)). Dünweg *et al.* [7] have calculated the lowest-order correction to be

$$\frac{D}{D_0} = \frac{1}{N} + \frac{a}{b} \left(\frac{A}{\sqrt{N}} - \frac{4.0364}{N} \right). \quad (3)$$

From this we see that in long polymers the hydrodynamic interactions between beads dominate the dynamics (eq. (2)). Furthermore, a short chain will not generally display the same scaling as a long one. Notably, only in the scaling limit is the ratio a/b irrelevant. This is a genuine effect that does influence the dynamics of short chains [7]. The problem is, it is only practical to simulate the long-time dynamics of polymers with short model polymers. If one is interested in the long-polymer scaling limit, deviations from scaling will be overemphasized.

How long a model polymer need be to reach this limit depends on the ratio a/b (eq. (1)). Equation (3) does suggest a value for a/b that might minimize this problem. Note that, for a “magic” value of the ratio of the Kuhn length to the hydrodynamic radius, $b = 4.04a$, the finite- N correction to the hydrodynamic contribution will cancel the non-hydrodynamic contribution and yield the scaling $D/D_0 \propto 1/\sqrt{N}$ for all N . That is, long-polymer scaling should hold, to a good approximation, even for short model polymers. In terms of polymer theory [8], this would correspond to the dynamic scaling limit being reached even with short polymers. The scaling will not hold exactly because there are higher-order corrections neglected in eq. (3). Using Monte Carlo methods, we have solved eq. (1) numerically and see that it does hold to a very good approximation (see fig. 1). For illustrative purposes, we have also plotted the result for $b = 8.08a$. It approaches asymptotic scaling only slowly. The result for $N = 64$ is still far from asymptotic.

Description of the model. – What we now want to do is find a way of modelling the effects of the solvent such that the hydrodynamic interactions between beads and thermal fluctuations are included. Furthermore, we want to be able to use the magic value of a/b so that we should have long-polymer scaling even with short model polymers. We also want to satisfy, as best as we can, the conditions on the relative magnitudes of the time scales we outlined above.

The approach we choose is to use a simple particle model for the solvent — a dissipative ideal gas. There are no static interactions between solvent particles so the solvent has an ideal-gas equation of state. The method has been used widely as a test case for dynamic particle models [9, 10], but little used as a practical tool. The model polymer consists of beads, with adjacent beads connected by a harmonic potential of the form

$$U = k_B T \sum_{i=1}^{N-1} \frac{3}{2b^2} (\vec{r}_i - \vec{r}_{i+1})^2. \quad (4)$$

This allows us to specify the Kuhn length. As the solvent is ideal, it will not influence the static properties of the chain. It remains exactly what we specify — an ideal chain. The solvent's role here is simply to mediate the hydrodynamic interactions between polymer beads.

The ideal-gas solvent is dissipative because total energy is not conserved. It is maintained at a constant temperature by a Lowe-Andersen thermostat [9]. Dynamically, the thermostat makes a contribution to the viscosity so it is possible to satisfy the condition for liquid-like ($D_s \ll \nu$) rather than gas-like ($D_s \sim \nu$) dynamics. Here D_s is the solvent diffusion coefficient. The Lowe-Andersen thermostat conserves momentum and is Galilean invariant. These are important pre-requisites for reproducing the correct hydrodynamics. In this respect, it is similar to dissipative particle dynamics (DPD) [2]. It has the advantage that a simple algorithm suffices to update the equations of motion and still satisfies detailed balance. In practice, this means that static properties of the system (temperature, Kuhn length, etc.) will be correct (so long as a time step short enough to adequately integrate the non-dissipative equations of motion is used [11]). The procedure simply consists of using a velocity Verlet algorithm to integrate the normal (conservative) equations of motion over a time-step Δt . Pairs of particles within a distance r_c (an interaction radius for the thermostat) of each other are identified. With a probability $\Gamma \Delta t$, the particles undergo “bath” collisions, in that their relative velocity along the line of centres is re-drawn from a Maxwellian. The individual particle velocities are then updated such that momentum is conserved. The bath collisions take on the role of the dissipative force in DPD. While simpler and more efficient than DPD when viewed purely as a thermostat, this method may seem a little cruder in that it does not involve a distance-dependent weight function for this dissipative interaction. However, in DPD this function is somewhat arbitrary and, as we will see, this does not seem to be a problem. The beads making up the model polymer have exactly the same dissipative interaction with surrounding solvent but do not interact with each other (the dynamic interaction between beads comes only through the springs and solvent). This means that we can, without ambiguity, identify the monomer diffusion coefficient as being the diffusion coefficient of the solvent particles ($D_s = D_0$).

Model parameters. – Despite its simplicity, the model still has a number of parameters we need to specify. Here we discuss the values we assign to them with a brief explanation as to why. The dissipative ideal gas itself is characterized by just two parameters. Firstly, a typical interparticle separation $\lambda = (1/\rho)^{1/3}$, where ρ is the number density. Secondly, a parameter $\Lambda = \sqrt{k_B T / (\Gamma^2 r_c^2 m)}$, where m is the solvent particle mass, characterizing the ratio of the time it takes particles to displace r_c to the mean bath collision time. With the polymer present

we have an additional parameter a/b . Considering r_c , it must be greater than λ , otherwise particles will rarely interact and will undergo prolonged ballistic motion. Large values of r_c are computationally inconvenient. A trade-off is required and we compromise on a value $r_c^3 = 6/(\pi\rho)$ (each solvent particle interacts, on average, with eight others). Decreasing Λ decreases the ratio τ_ν/τ_D , but also increases the ratio $\nu/(\lambda c_s)$. That is, the sonic time starts to become significantly longer than the viscous time. This is inconsistent with what we ideally require. The value we have used is $\Lambda = 0.03$ which gives $\nu/D_s = 60$, so for the polymer $\tau_D/\tau_\nu > 60$, and, based on a characteristic length of a particle separation, $\tau_\nu/\tau_s = 0.26$. Therefore, on a solvent length scale, the system is somewhat too compressible. The final parameter we need to specify is the Kuhn length. For small values of Λ , we find that the hydrodynamic radius of the solvent particles (based on their diffusion coefficient) is $a = 0.21\lambda$, independent of Λ . This means that the magic ratio corresponds to $b \approx 4a = 0.84\lambda$. That is, a typical polymer bead separation must be of the order of, or less than, a typical solvent particle separation.

Results. – The simulations were carried out using 10^4 solvent particles and chains consisting of $N = 2, 4, 8, 16$ and 32 beads. The Lowe-Anderson thermostat has a maximum time-step ($\Gamma\Delta t = 1$) and we used half this value. The polymer temperature and Kuhn length calculated from the simulations were, to the accuracy we calculated them ($> 0.1\%$), the same as the set values. From the data, we calculated the centre-of-mass velocity autocorrelation function (VCF),

$$C(t) = \frac{1}{3N^2} \left\langle \left(\sum_{i=1}^N \vec{v}_i(0) \right) \cdot \left(\sum_{i=1}^N \vec{v}_i(t) \right) \right\rangle, \quad (5)$$

from which we in turn derived the centre-of-mass diffusion coefficient

$$D(t) = \int_0^\infty C(t) dt. \quad (6)$$

The first thing we want to look for is any spurious consequence of the solvent being too compressible. In fig. 2 we have plotted the function $C(t)$ in dimensionless form ($C(t)m/(kT)$, where m is the mass of the polymer), as a function of dimensionless time $tkT/(mD)$. The time is thus measured relative to the polymer inertial time (the time scale on which centre-of-mass velocity correlations would decay, according to a simple Langevin equation). Taking the radius of gyration of the polymer r_g as the characteristic length scale $l = r_g = \sqrt{Nb^2/6}$, by varying N we are varying both the ratio $\tau_s/(\tau_\nu)$ and τ_ν/τ_D (because $\tau_s \propto \sqrt{N}$, $\tau_\nu \propto N$ and $\tau_D \propto N^{3/2}$). However, the results rapidly become indistinguishable for $N > 4$. That is, the fact that these ratios do not take the correct values is inconsequential. Where the results fall onto one curve this is the true curve for *any* ideal chain because it is independent of N . It is not so obvious that the excessive compressibility of our solvent should not perturb the results on short time scales. Indeed, Malevanets and Yeomans [3] developed a theory to describe the deviations from exponential decay that they observed by taking into account compressibility.

Theories that do not take into account the time dependence of the hydrodynamic interactions predict that the decay of the VCF is exponential (see fig. 2). Examining the functional form of the decay we find that it is not exponential, at either short or long times. We believe this reflects the fact that the model does include the time dependence of the hydrodynamic interactions. The VCF is plotted in ln-ln form in fig. 3. Also shown is the asymptotic decay $C(t) \sim t^{-3/2}$ recently predicted by a theory that takes this time dependence into account [12]. This is an algebraic “long-time tail” of exactly the same form one observes in the VCF for solid particles [6]. The scaling we observe, however, implies somewhat different behaviour of

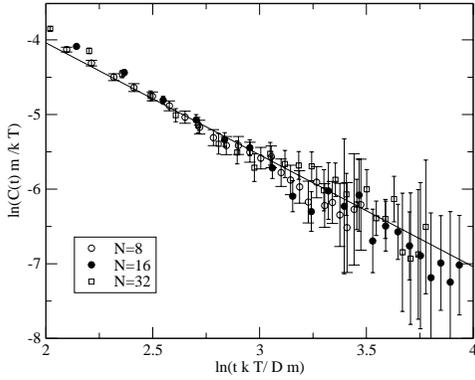


Fig. 3

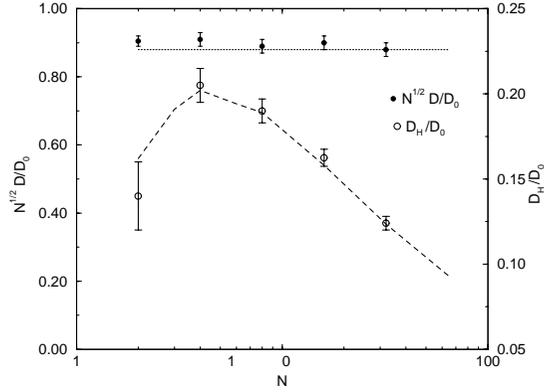


Fig. 4

Fig. 3 – Ln-ln plot of the normalized velocity autocorrelation function at long times for chains with different number of beads N . The solid line shows $t^{-3/2}$ decay.

Fig. 4 – Polymer diffusion coefficient D and the hydrodynamic contribution to the diffusion coefficient D_H calculated using chains of 2, 4, 8, 16 and 32 beads. The upper (dotted) line is the theoretical asymptotic ($N \rightarrow \infty$) result for D . The lower dashed line is the theoretical result for D_H as a function of N .

the characteristic time for the asymptotic decay in the case of a polymer. For a solid particle the normalized VCF decays as a unique function of the dimensionless time $\tau_c = \rho^* a^2 / \nu$, where a is the particle radius and ρ^* the ratio of the density of the solid particle to the density of the fluid. For colloidal particles this is always close to unity. Here, by contrast, we find a characteristic time $\tau_c = k_B T / (Dm)$. If we suppose the polymer occupies a spherical volume of radius r_g and introduce a polymer density $\rho_p = m/r_g^3$, this characteristic time is $\tau_c = \rho_p r_g^2 / (\rho \nu)$. That is, the scaling of the decay for a polymer is of the same form as that for a solid particle if we allow for the fact that a polymer is less dense than the equivalent volume of solvent. The difference between the two cases increases with increasing N because ρ_p / ρ scales as $1/\sqrt{N}$. Thus, the long-time tail for a polymer is a relatively weaker affair when compared to the long-time tail of a solid particle of equivalent dimension.

Turning to the actual values of the diffusion coefficient, in fig. 4 we have plotted $\sqrt{N}D/D_s$ as a function of N . In contrast to other workers (probably because we are in a different parameter regime), we do not need to apply any finite-size corrections because D asymptotes on a time scale that is still short compared to the time it takes hydrodynamic interactions to propagate between periodic images. Note that, to within the errors, $\sqrt{N}D/D_s$ is a constant. As we know, this is also the asymptotic result (shown in the figure) we can conclude that long-polymer scaling $D \propto 1/\sqrt{N}$ holds to an excellent approximation for model polymers even as small as $N = 2$. We remarked that for values of the Kuhn length similar to a solvent interparticle separation, it would be surprising if the model adequately resolved the hydrodynamics. The most sensitive test of this is to look at the hydrodynamic contribution to the diffusion coefficient D_H (almost any model will get the Rouse-like contribution in eq. (1) right by construction). That is

$$\frac{D_H}{D_0} = \frac{D}{D_0} - \frac{1}{N}. \quad (7)$$

The values we calculated are also shown in fig. 4. As the figure shows, we find no statistically significant difference between the numerical values and the theoretical value. We should point

out though that, allowing for the errors, for $N=2$ this means that the maximum possible discrepancy would be 15%. However, for $N=4$ this is 6% and by $N=8$ it is 4%. The model clearly does a remarkably good job of resolving the hydrodynamics even on very short length scales.

Discussion. – We have considered the dynamics of a single model polymer for which, theoretically, we know the values for the diffusion coefficient. In this sense it is a test case. For many polymer systems or flows in complex geometries there is of course no analytic solution and a numerical model is required. Once validated, this would be the point of such a model.

We have shown that by choosing a particular magic value of the ratio of the Kuhn length to the monomer hydrodynamic radius a model polymer displays long-polymer scaling of the diffusion coefficient for all numbers of monomers. In this sense one imposes dynamic scaling, to a good approximation, even for short polymers. Using a very simple model solvent we reproduced this scaling numerically. This is because the model gives an excellent description of the hydrodynamics even on length scales comparable to a typical solvent particle separation. Examining the time scales associated with the polymer solvent model we showed that in order to separate the diffusive and viscous times the solvent must be more compressible than a real system. However, we also showed that this does not influence the dynamics so cannot be considered problematic.

Using the model it was possible to show that the centre-of-mass dynamics of a long ideal chain could be calculated using short chains. The function does not decay exponentially but with an algebraic long-time tail of the form predicted by theories that take into account the time dependence of the hydrodynamic interactions. If allowance is made for the fact that the polymer is much less dense than the solvent, the characteristic time for this decay is analogous to that of a solid particle of equivalent size. This actually implies something quite interesting. One would normally expect that hydrodynamic interactions propagate by momentum diffusion. It would take times of the order $\tau_{\text{HI}} \sim r_{\text{g}}^2/\nu$ for them to fully propagate between all the monomers. This time scales as $\tau_{\text{HI}} \sim N$. However, the characteristic time for the decay of the VCF scales as $\tau_{\text{c}} \sim \sqrt{N}$. The time-dependent diffusion coefficient asymptotes on this time scale and its value reflects the effect of all the intra-monomer hydrodynamic interactions (eq. (1)). Consequently, these interactions must have propagated between all beads in the polymer on this time scale. But, for a long polymer, the above analysis gives $\tau_{\text{c}} \ll \tau_{\text{HI}}$, which cannot be the case. The intra-chain hydrodynamic interactions must propagate on a more rapid time scale than we surmized. The origin of this effect is a subject for further research.

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