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Scaling laws for polymers in dissipative particle dynamics

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Abstract. – A new technique, dissipative particle dynamics (DPD), appears promising as a means of studying the dynamical behaviour of polymers. Real polymers are known to obey a number of scaling laws, and a simulation method should reproduce these if it is to be relied on. The present work is a study of the properties of polymers, as simulated by DPD. Two cases are of interest: polymers in dilute solution, and polymers in the melt. The polymer in a good solvent shows satisfactory agreement with scaling and Kirkwood theory, and the polymer melt is in excellent agreement with the predictions of Rouse theory.

Introduction. – A new technique, dissipative particle dynamics (DPD), has been proposed as an alternative to molecular dynamics for studying hydrodynamics in colloidal systems. The original DPD algorithm due to Hoogerbrugge and Koelman [1] was shown not to obey detailed balance, and a modified scheme was proposed by Español and Warren [2]. This new algorithm is fully consistent with statistical mechanics, and appears well suited to studying phenomena where we must capture both thermodynamic and hydrodynamic effects. It has already been used to study spinodal decomposition [3, 4] and the rheology of colloidal suspensions [5, 6], but it appears particularly appropriate for polymer problems, such as the phase behaviour and evolution of block copolymer melts [7, 8], and the rheology of dilute polymers in confined geometries [9] and different solvent conditions [10–12]. Real polymers are known to obey a number of scaling laws, and a simulation method should reproduce these if it is to be relied on. The present work is a study of the properties of polymers, as simulated by DPD. Two cases are of interest: polymers in dilute solution, and polymers in the melt.

DPD is a Langevin dynamics scheme, in which we simulate a fluid of particles interacting through conservative, random and dissipative forces. The conservative forces determine the equilibrium state of the system. The dissipative and random forces have two effects: they act as a thermostat, and they allow transport properties such as viscosity to be tuned without altering the equilibrium thermodynamics. Note that all of these forces are taken to be pairwise and satisfy Newton's Third Law, and as a consequence of this, hydrodynamic modes are preserved (*i.e.* the system obeys the Navier-Stokes equation in the limit of long times and wavelengths) [13]. This is different from ordinary Brownian dynamics, in which the dissipative forces act relative to a fixed background, and where the particles move diffusively.

The algorithm used in the present work is identical to that of refs. [2, 7] (the notation follows that of ref. [7]). The particles obey Newton's equations:

$$\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} = \boldsymbol{v}_i, \quad m\frac{\mathrm{d}\boldsymbol{v}_i}{\mathrm{d}t} = \boldsymbol{f}_i\,, \tag{1}$$

where the forces are a sum of three contributions:

$$\boldsymbol{f}_i = \sum_{j\neq i}\left(\boldsymbol{F}_{ij}^{\mathrm{C}} + \boldsymbol{F}_{ij}^{\mathrm{D}} + \boldsymbol{F}_{ij}^{\mathrm{R}}\right)\,. \tag{2}$$

The conservative component is taken to be linear up to a cut-off in particle separation r_c, and zero outside of this:

$$\boldsymbol{F}_{ij}^{\mathrm{C}} = \begin{cases} a(1-r_{ij}/r_\mathrm{c})\hat{\boldsymbol{r}}_{ij} & (r_{ij} < r_\mathrm{c})\,, \\ 0 & (r_{ij} \geq r_\mathrm{c})\,, \end{cases} \tag{3}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, $r_{ij} = |\boldsymbol{r}_{ij}|$, $\hat{\boldsymbol{r}}_{ij} = \boldsymbol{r}_{ij}/|\boldsymbol{r}_{ij}|$, and a is a constant. Note that there is no hard-core divergence of the force, as with, *e.g.*, the Lennard-Jones potential. This makes for a rather efficient scheme, since such a soft force law allows a large time step. The other forces are

$$\begin{aligned} \boldsymbol{F}_{ij}^{\mathrm{D}} &= \quad -\gamma w^{\mathrm{D}}(r_{ij})(\hat{\boldsymbol{r}}_{ij}\cdot\boldsymbol{v}_{ij})\hat{\boldsymbol{r}}_{ij}, \\ \boldsymbol{F}_{ij}^{\mathrm{R}} &= \quad \sigma w^{\mathrm{R}}(r_{ij})\theta_{ij}\hat{\boldsymbol{r}}_{ij}\,, \end{aligned} \tag{4}$$

where $\theta_{ij}(t)$ is a delta-correlated Gaussian random variable ($\langle\theta_{ij}(t)\rangle = 0$ and $\langle\theta_{ij}(t)\theta_{kl}(t')\rangle = (\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\delta(t-t')$); we must have $w^{\mathrm{D}}(r) = [w^{\mathrm{R}}(r)]^2$ and $\sigma^2 = 2\gamma k_\mathrm{B}T$ for detailed balance, and we take [2]

$$w^{\mathrm{D}}(r) = [w^{\mathrm{R}}(r)]^2 = \begin{cases} (1-r/r_\mathrm{c})^2 & (r < r_\mathrm{c})\,, \\ 0 & (r \geq r_\mathrm{c})\,, \end{cases} \tag{5}$$

There is a natural generalisation to more than one species of particle [7, 14]. The units are conveniently taken as $m = k_\mathrm{B}T = r_\mathrm{c} = 1$.

In ref. [7], some equilibrium properties of the DPD polymer melt are studied (interfacial tension and χ-parameter) and here the same model of a polymer is used. A polymer is modelled by connecting ordinary DPD particles with springs to make a chain. The algorithm is identical to that above, except that now additional spring forces $\boldsymbol{F}^{\mathrm{S}}$ act between adjacent particles in a chain. The present work uses a linear spring $\boldsymbol{F}_{ij}^{\mathrm{S}} = -k\boldsymbol{r}_{ij}$, but other choices are possible [15].

Polymers in the melt. – We expect the DPD polymer melt to be described by the Rouse theory [16]. In fact, the Rouse model is very close to the DPD melt; the essential difference is that in DPD, we have explicitly a many-chain problem with excluded volume and hydrodynamic interactions which we expect to be screened out, whereas in Rouse theory, excluded volume and hydrodynamics are assumed to be screened out and simply omitted.

I have carried out simulations to measure R_0, τ and D for DPD polymers in the melt. In these calculations, N, the number of DPD particles in the polymer, was varied between 2 and 100. The box size was 10^3 for the shorter polymers and 15^3 for the longer, the density of particles was 3, the interparticle repulsion a was 25, and the noise strength σ was 3.35 (in

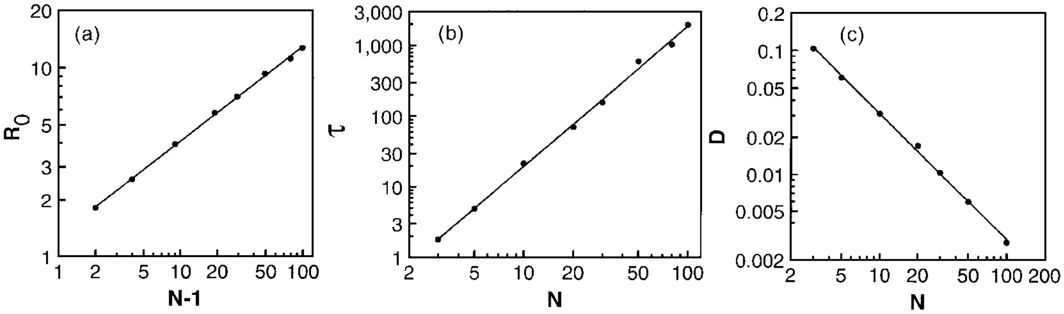

Fig. 1 – (a) R_0, (b) τ and (c) D for the polymer melt.

natural units $m = k_{\mathrm{B}}T = r_{\mathrm{c}} = 1$). All the particles were part of a polymer, *i.e.* there were no solvent or free monomers. Adjacent particles on a polymer backbone interacted via a linear spring, with spring constant k of 2. The equations of motion were integrated using the Verlet method, as described in ref. [7], and the time step was 0.05, which gave a kinetic temperature within 1% of the nominal value. The simulations required 0.8 s of CPU time per time step per 10000 particles (on a Silicon Graphics R10000 processor).

The autocorrelation function of the end-to-end vector is asymptotically an exponential, and the terminal relaxation time τ is extracted by fitting. The diffusion coefficient is measured by calculating the mean-square displacement of the centre-of-mass coordinate $\langle(\boldsymbol{R}_{\mathrm{CM}}(t) - \boldsymbol{R}_{\mathrm{CM}}(0))^2\rangle$ which tends to $6Dt$ for times longer than τ.

The measured quantities R_0, τ and D are shown in fig. 1. R_0 is shown as a function of $N-1$, whilst D and τ are plotted against N. We expect D to be inversely proportional to N, because in the free-draining limit, the drag is just proportional to the number of beads. There is a more complicated behaviour for τ: according to Rouse theory, it is proportional to $1/\sin^2(\pi/2N)$ for finite N, but this is close to N^2 except for small N [17]. The power law fits are shown as solid lines on the graphs, and are numerically as follows:

$$R_0 = (1.30 \pm 0.02)(N-1)^{0.498\pm0.005}\,, \tag{6}$$

$$\tau = (0.20 \pm 0.03)N^{1.98\pm0.03}\,, \tag{7}$$

$$D = (0.33 \pm 0.02)N^{-1.02\pm0.02}\,. \tag{8}$$

Note that these reproduce exactly the scaling behaviour predicted by Rouse theory. Since the theory has only two free parameters, and we have measured three quantities, we can also test the prefactors. According to the theory, $D = R_0^2/3\pi^2\tau$ for large N. Using the fits for R_0 and τ, this gives $D = (0.29 \pm 0.04)/N$, compared with the number above fitted to the simulation.

By using Lees-Edwards boundary conditions, we can simulate a shear flow and calculate the viscosity of the melt (an alternative method would be to use the equilibrium simulations and a Green-Kubo formula [18]). The stress tensor is [18]

$$\boldsymbol{\sigma} = \sum_i m\boldsymbol{v}_i\boldsymbol{v}_i + \sum_{ij}\boldsymbol{r}_{ij}\boldsymbol{F}_{ij}^{\mathrm{C}} + \sum_{ij}\boldsymbol{r}_{ij}\boldsymbol{F}_{ij}^{\mathrm{S}} + \sum_{ij}\boldsymbol{r}_{ij}\boldsymbol{F}_{ij}^{\mathrm{D}}\,. \tag{9}$$

Figure 2(a) shows the shear stress as a function of the shear rate, for the 50-mer. The shear rate is given in units of the (reciprocal) Rouse time for a polymer of this length. Note that

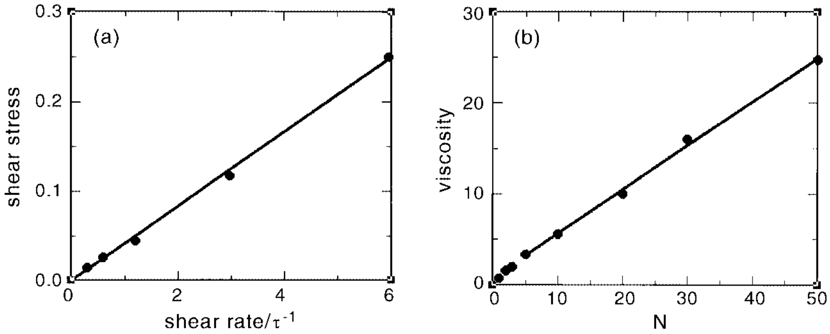

Fig. 2 – (a) Shear stress in a 50-mer melt, (b) viscosity of the polymer melt as a function of molecular weight N.

the shear stress is linear in shear rate even at fairly high shear rates, in agreement with Rouse theory. Figure 2 (b) shows the viscosity as a function of N, which is clearly linear and fitted by

$$\eta = (0.8 \pm 0.4) + (0.48 \pm 0.01)N\,. \tag{10}$$

Again, we can use Rouse theory to check the prefactor. The prediction is $\eta = (\pi^2/12)\rho k_{\mathrm{B}} T\tau/N$ for large N, where ρ is the concentration of monomers ($\rho = 3$ in the present work). This gives $\eta = (0.49 \pm 0.07)N$, in agreement apart from the constant term which lies outside the scope of the theory.

I found no evidence for entangled behaviour in any of the simulations described in this work: the viscosity, diffusion coefficient and relaxation time obey the power laws predicted by Rouse theory up to the highest molecular weight tested ($N = 100$), despite the fact that MD studies of Lennard-Jones and hard sphere polymers did find entanglement [19–21]. It is likely that DPD polymers cannot show entangled behaviour at all. Since there is no hard-core repulsion, it is possible for the chains to pass through each other. A simple test of this is possible. I simulated a pair of ring polymers (of 10 beads each), which are interlinked at the start of the simulation. After a few time units (*i.e.* within one relaxation time) the rings separate, indicating that there is no effective barrier to chain crossing. This happens whether the remaining space is filled with solvent or with other polymers.

Polymer in dilute solution. – I have carried out simulations of a single polymer in a box of a solvent, and measured the r.m.s. end-to-end length and the relaxation time. The solvent consisted of particles identical to the monomer, *i.e.* the athermal solvent, which is a special case of a good solvent. The effect of varying the solvent quality, *i.e.* changing the strength of the interaction between the polymer and the solvent, was not investigated in the present work.

Figure 3 shows R_0 and τ as a function of N. The errors are somewhat greater than for the melt: this is because it is possible in the melt to average over all of the polymers in the simulation. The power law fits are

$$R_0 = (1.13 \pm 0.17)(N-1)^{0.58\pm0.04}\,, \tag{11}$$

$$\tau = (0.25 \pm 0.04)N^{1.80\pm0.04}\,. \tag{12}$$

The shortest polymers are excluded from the fit, because they are expected to deviate from the power law behaviour of the long polymers. These results show quite satisfactory agreement

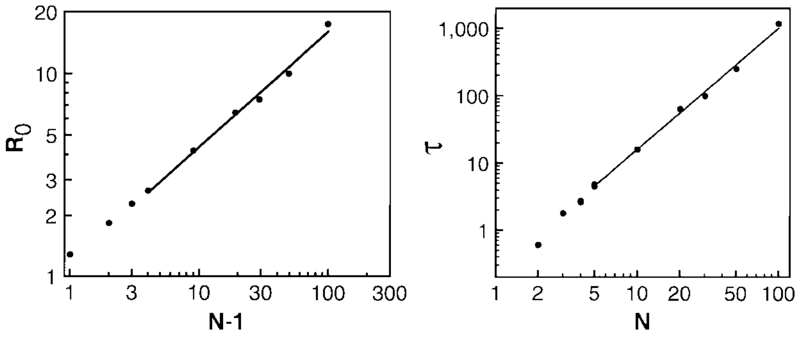

Fig. 3 – (a) R_0 and (b) τ for the polymer in dilute solution.

with the classical result ($R_0 \propto N^{0.59}$, $\tau \propto R_0^3$) [22] and indicate that the DPD polymer shows the correct equilibrium thermodynamics and hydrodynamics for a dilute solution in good solvent.

The diffusion coefficient cannot be measured directly, since it is rather sensitive to the size of the simulation box (the finite-size correction is of order $1/L$ [23]). However, it is possible to make a comparison with theory using the method of Dünweg and Kremer [23], which is based on Kirkwood's theory. The beads are assumed to interact via the Oseen tensor, giving the short-time diffusion coefficient as

$$D = \frac{D_0}{N} + \frac{k_B T}{6\pi\eta N^2} \sum_{i \neq j} \left\langle \frac{1}{r_{ij}} \right\rangle , \tag{13}$$

where D_0 is the monomer diffusion coefficient, η is the solvent viscosity and the sum is taken over all pairs of monomers. We know the static structure of the polymer from the simulation, so we can calculate the diffusion coefficient in the periodic geometry by extending the sum to the periodic images. In practice, this is conveniently done by evaluating an Ewald sum [23,24].

Figure 4 shows the diffusion coefficient predicted in this way, as well as the diffusion coefficient measured directly from the centre-of-mass mean-square displacement, for chains of

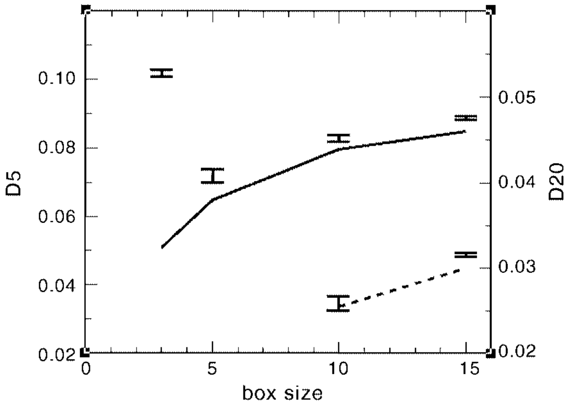

Fig. 4 – Diffusion coefficient calculated from the Kirkwood theory (lines) and measured directly (bars), for 5-mers (solid line, left y-axis) and 20-mers (dashed line, right y-axis).

$N = 5$ and $N = 20$. The solvent viscosity is 0.88, and we take D_0 to be the same as the solvent diffusion coefficient (0.30). The agreement is quite good, especially for the longer polymer. The large value of D for a box size of 3 is possibly due to the granularity of the solvent (there are only 81 particles in the simulation), an effect which lies outside the scope of the Kirkwood theory.

There is another effect that might play a role. The Kirkwood theory assumes that the hydrodynamic interaction acts instantaneously. This is correct for a real liquid such as water, in which the ratio of the kinematic viscosity to the diffusion coefficient (sometimes called the Schmidt number) is large. In the present DPD simulation, the Schmidt number is about one, so in principle we expect corrections to the Kirkwood theory. However, recent work suggests that the effect of the finite Schmidt number is small [25], and this is borne out by the present results.

DPD polymers in solution have previously been studied by Kong, Manke, Madden and Schlijper [10–12, 15]. They measured the radius of gyration, relaxation time, viscosity and first normal stress coefficient, and studied the effect of solvent quality and confinement between solid surfaces. They reported a scaling exponent of 0.52 for an athermal polymer, by comparison with 0.59 expected from theory (and found in the present study to within the errors). The discrepancy may be due to the type of spring used [26]. The polymer end-point distribution in the melt has been studied by Groot *et al.* [27] for a single molecular weight (10). They found an exponent of 0.54 for the polymer melt and verified that the distribution is Gaussian.

Conclusions. – I have investigated the properties of polymer melts and solutions in DPD. DPD polymers are "phantom chains" which pass freely through each other. The polymer in good solution is in satisfactory agreement with scaling theory and the Kirkwood theory; in particular, it reproduces the scaling exponent for self-avoiding chains. The polymer melt is in excellent agreement with the predictions of Rouse theory.

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