

Abstract

- The properties of polymer diffusion over time can be experimentally determined and simulated for a pure polymer melt. The pure polymer diffusion coefficient D_0 is calculated from the centre of mass variation in a Monte Carlo Model.
- Polymer properties change with the introduction of NP's into the polymer melt. High surface to volume ratio of NP's efficiently change the behaviour of diffusing tracer polymers. NP's produce an entropic barrier reducing polymer conformations.
- Understanding how polymers diffusion properties change in the presence of NP's entropic barriers is applicable to many biological processes such as the folding of molecules within cell cytoplasm or the delivery of virus DNA into a host nucleus.

Polymer Dynamics

Consider fig.1a a polymer of length R_e initially extended out in a pure polymer melt, after a period of time diffusion will cause this polymer to naturally reach an equilibrium state similar to that in figure 1b. L_{e2e} is the end to end distance of the polymer and R_g is the radius of gyration, a property which defines the radius of conformations of the polymer. T_{Sub} is the time taken for the polymer to reach equilibrium. ^[1]

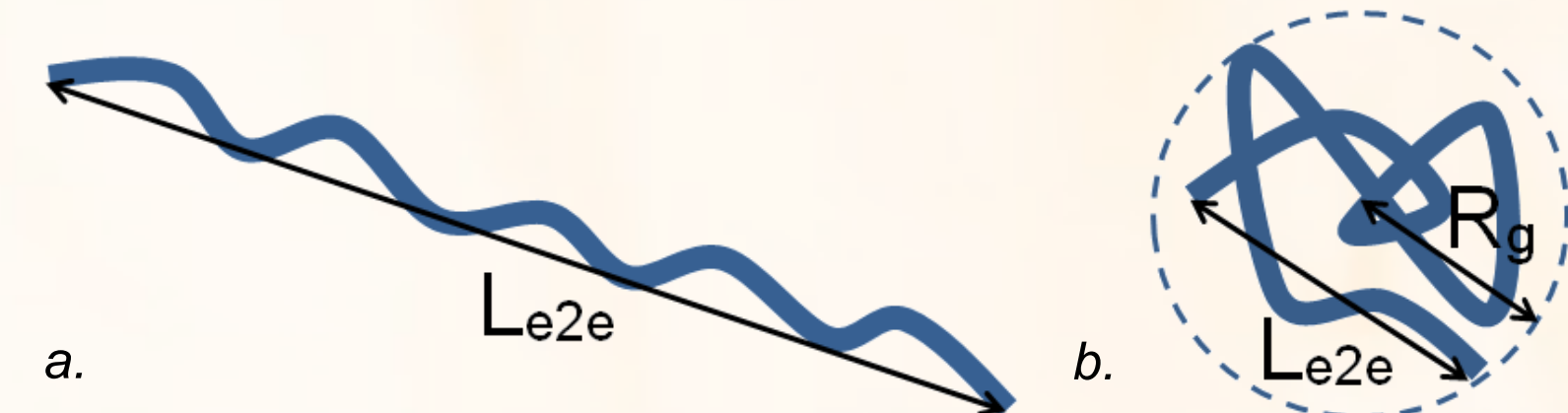


Fig 1. a, Initialised polymer out of equilibrium. b, A polymer in equilibrium

Fig.2a shows how the polymer can be thought of as contained within an initial tube where its diffusion within the tube is limited only to the movement of the ends of the polymer or the 'wiggling' of any kinks and bends along the length the polymer, this is known as sub-diffusivity. T_{Dif} is the time taken for reptation ^[1], where the polymers COM diffusion is completely free of its initial tube, as shown in fig. 2b.

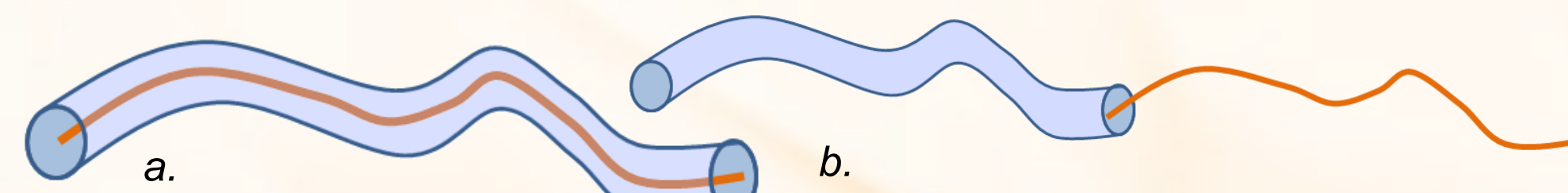


Fig 2. a, Initialised polymer within tube. b, A polymer after tube renewal, reptation

A polymer can be considered as a set of particles diameter b connected to each other contained within a tube. In order to model particle movement within a computer simulation the polymers chain lengths ' b ' are connected between nodes n where the number of nodes $n = N + 1$ and is N the number of polymer chains. This leads to expression for the average length and the square average length of many polymers;

$$R_e = Nb, \quad \langle R_e \rangle = 0, \quad \langle R_e^2 \rangle = Nb^2$$

The node-polymer bead model is visualised below in fig.3, where the spatial coordinates $r(x,y,z)$ of the polymer chain are stored on the nodes, therefore L_{e2e} is calculated by;

$$L_{e2e}^2 = (r_f - r_i)^2 \quad (\text{Eq. 1})$$

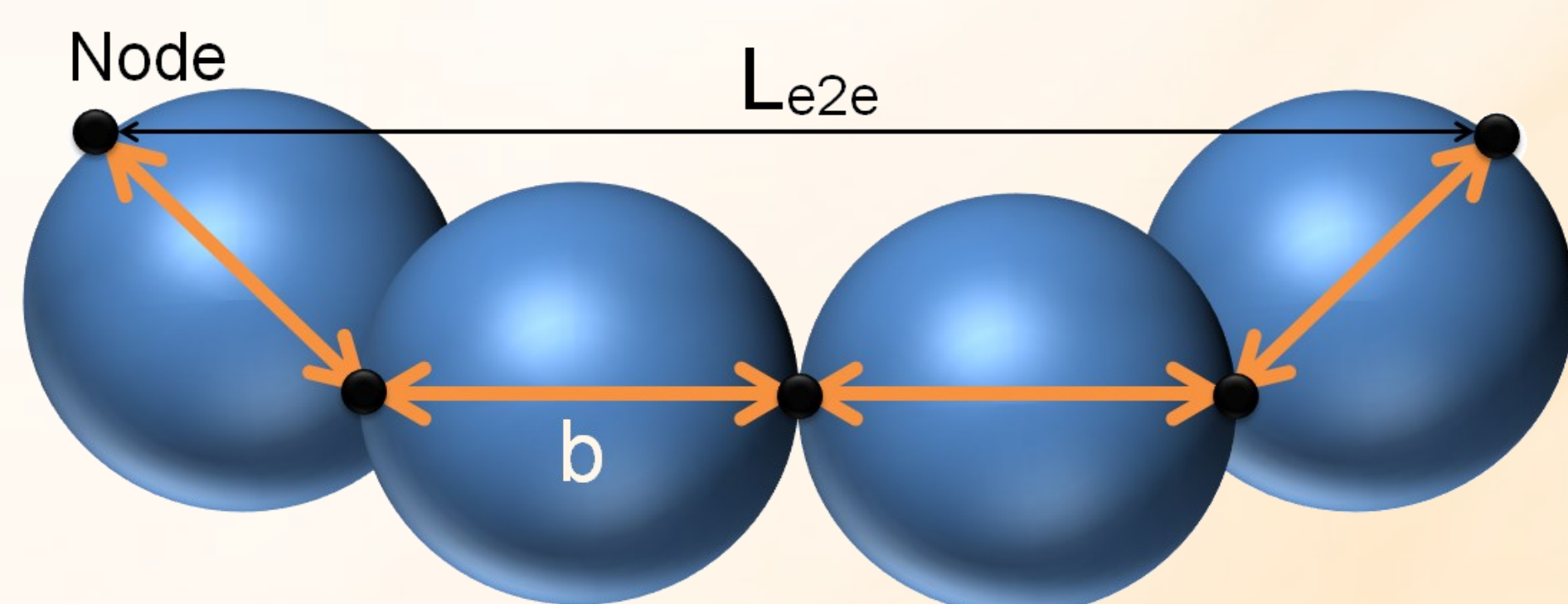


Fig 3. Node polymer bead model, a single chain of polymer connects adjacent nodes

Monte Carlo Model

Our Monte Carlo (MC) simulation emulates polymer diffusion via Brownian motion by randomly picking a polymer connection point node n_i . That position is moved in the case of;

- It being the end or start of the polymer (Pivot point next to end/start)
- It being the turn of a hairpin (Pivot point hairpin base)

This is equivalent to the polymer using kinks along its length to 'wriggle' free of its initial position. Fig. 4 demonstrates how a 2D model polymer can overlap and contain hairpins.

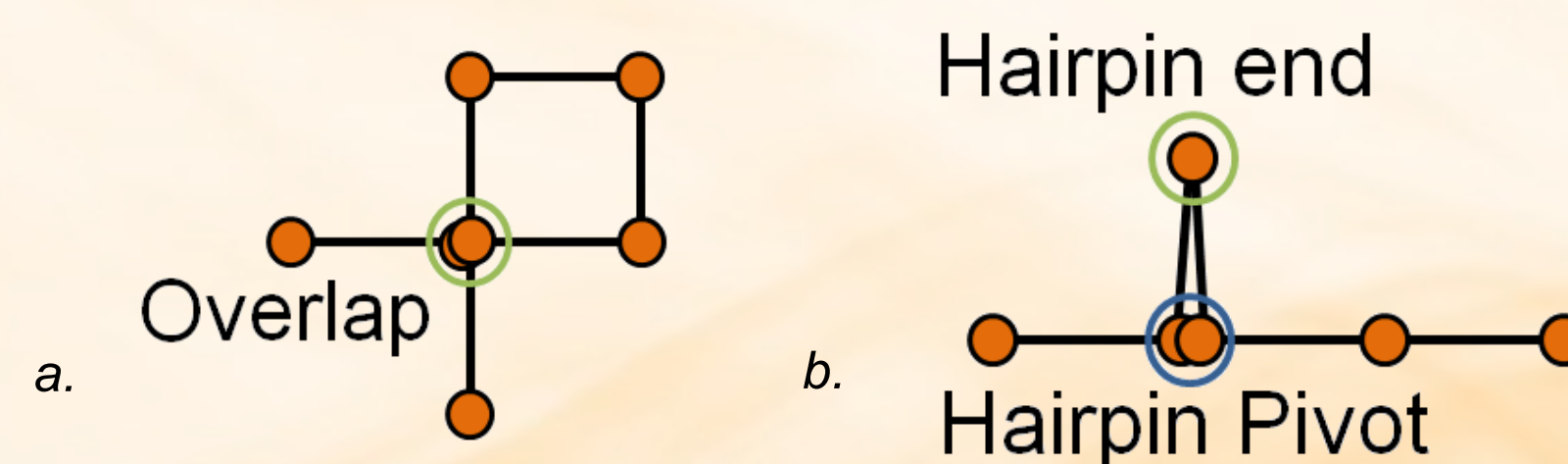


Fig 4. a, MC Polymer overlap. b, A MC hairpin bend

The polymer connection point is moved from its current node to any adjacent node around the moment pivot point (including its original position). Every potential direction has $P(1/6)$. The pictorial 2D grid example in fig. 5 shows a polymer of length $N = 4b$ with 5 nodes. The polymer starts at the node labelled 1, finishes at 5 and the polymer overlaps at the node where 2 and 4 are placed, causing a hairpin with the hairpin turn at node labelled 3.

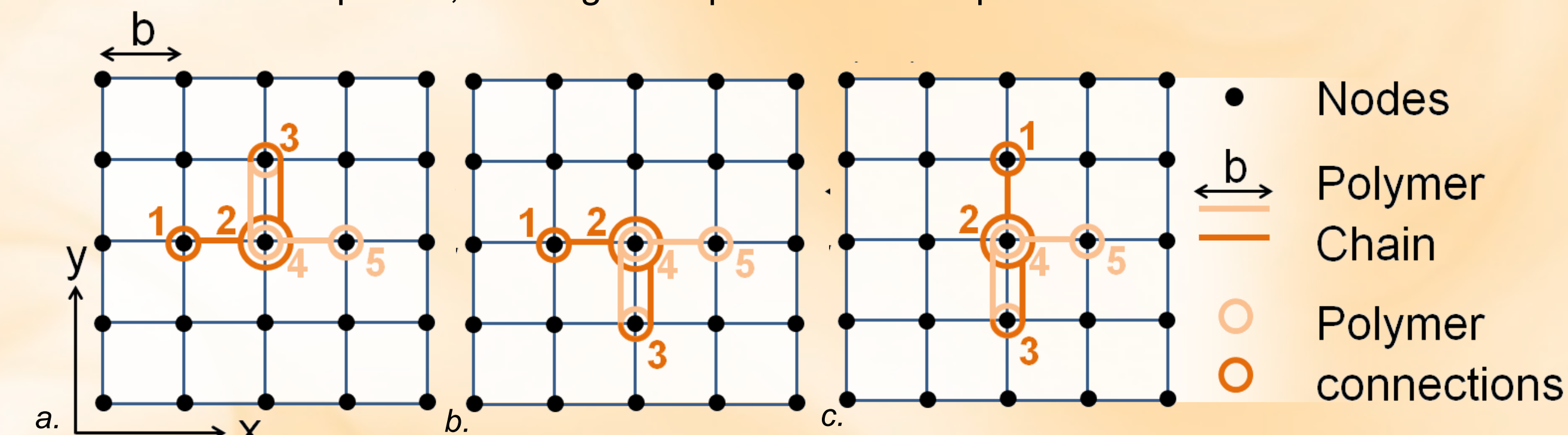


Fig 5. a, Initial setup. b, Hairpin move. c, Start of Polymer move. d, 3D hairpin

5a. shows an initial position. 5b. is after polymer hairpin end 3 has moved two nodes down from initial node. 5c. Is after polymer start 1 has moved one node right and two nodes left. In the 3D case, movement occurs in any of the six directions corresponding to an increase or decrease b from the pivot point in any of the three coordinates. (Fig 5d.)

Equilibrium & Sub-Diffusivity

A 3d MC simulation averaged over 250 polymers is performed with nodes upon positions $r(x,y,z)$ for various polymer lengths N . Data is recorded over T_{MC} , a MC time step defined by the amount of random walks it averagely takes for every polymer connection point along the length of the polymer to have moved; $T_{MC} = N$ 'random walks'. Theoretically $L_{e2e} \xrightarrow{T_{sub}} N^{0.5}$ ^[1]

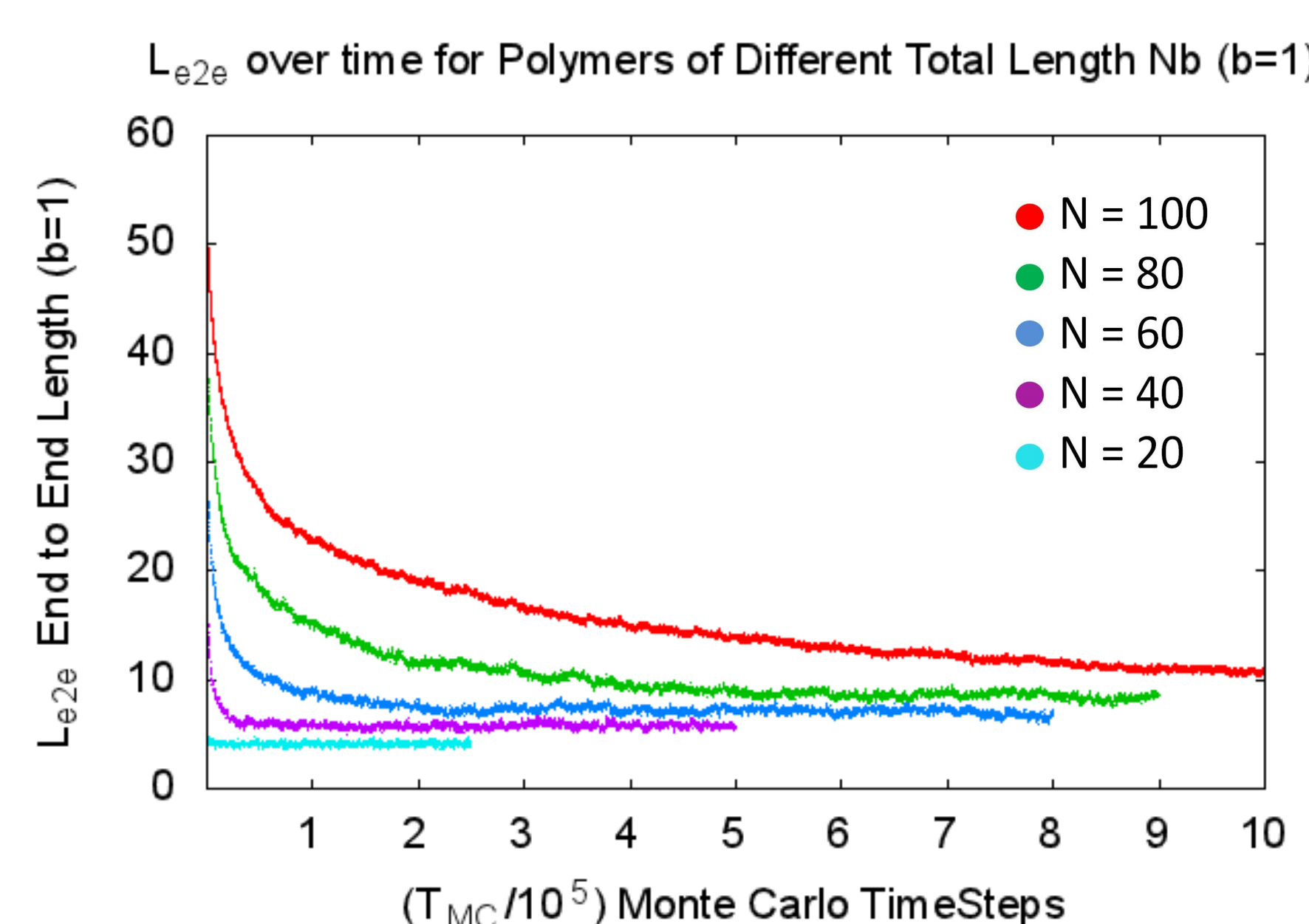
L_{e2e} is calculated Using eq 1. As expected fig 6. shows the polymers reach an equilibrium in which L_{e2e} asymptotes in the regime;

$$t > T_{Sub}$$

Fig 6. L_{e2e} for $N = 20 \rightarrow 100$

$N = 20$ reaches sub-diffusivity within 10^3 time steps, whilst $N=100$ has not fully reached equilibrium even after 10^6 . T_{Sub} is of the form;

$$T_{Sub} = 1.66 N^2 \quad [1]$$



Pure Melt Diffusivity - D_0

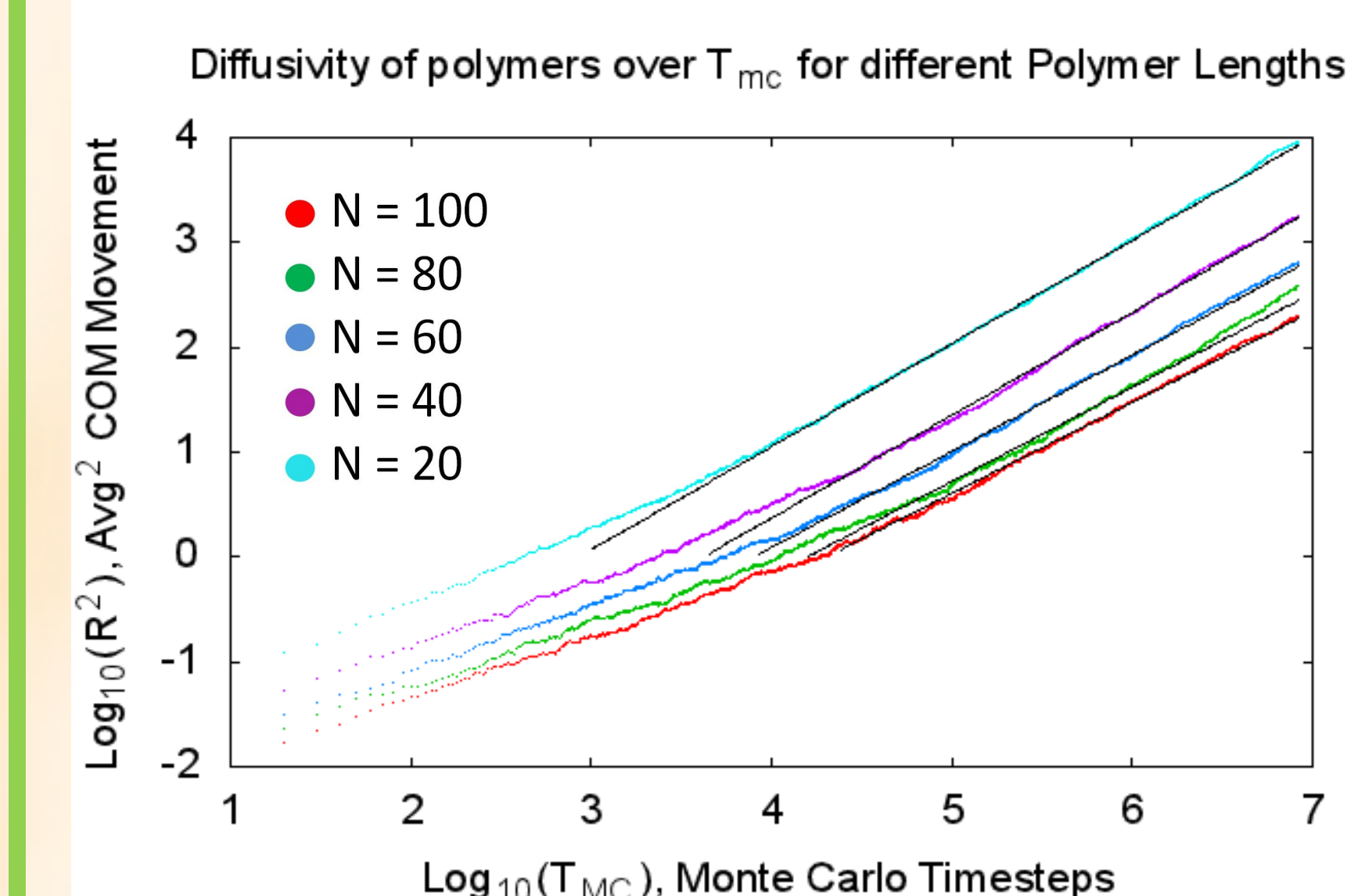
Once in equilibrium the MC polymers sub-diffusive behaviour can be analysed though the variation of their Centre of Mass (COM) position;

$$R_{cm} = \frac{1}{N} \sum_{i=1}^n r_i \quad (\text{Eq. 2})$$

Where eventually the MC polymers will reach reptation at which point for $t > T_{Dif}$ their whole length including COM will freely diffuse under the relation;

$$R^2 = \langle (R_{cm(T_{MC})} - R_{cm(0)})^2 \rangle \xrightarrow{T_{MC} \rightarrow \infty} DT_{MC} \quad (\text{Eq. 3}) \quad [1]$$

Figure 7 presents R^2 average COM movement over large T_{MC} timescales to show the transformation from sub-diffusive to diffusive behaviour where R^2 scales linearly with D .



The transition from sub-diffusive to diffusive is clearer for smaller polymers as it occurs after fewer time steps, but within $10^7 T_{MC}$ even MC polymer $N=100$ is demonstrating free centre of mass diffusion.

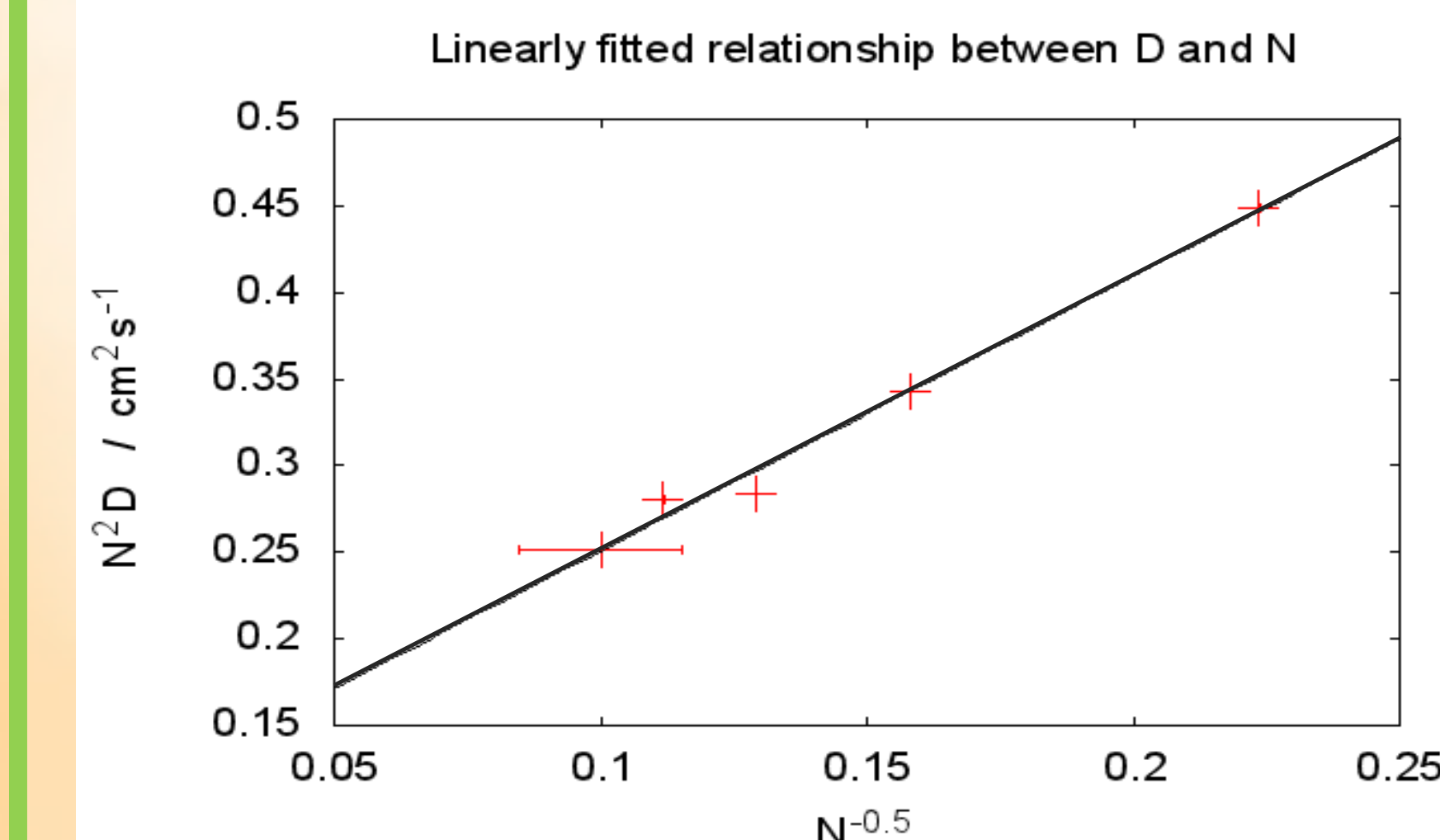
Fig 7. COM mass movement beyond equilibrium, polymers enter diffusive regime at T_{MC} $T_{Dif} = 2.62N^3$ ^[1]

As suggested by eq.3 Diffusivity is obtained from the gradients of fig 7. This is pure polymer melt diffusivity D_0 in units cm^2s^{-1}

The MC relation between D & N matches previous simulations, where for $t > T_{Dif}$. ^[2]

$$D \sim N^{-2.5} \quad (\text{Eq. 4})$$

Fig 8. Scatter showing strong correlation between D and N



Project Future

The MC model shall be extended to investigate the addition of NPs into the polymer melt with concentration Φ and inter-particle distance l_D . This extension shall simulate the effects shown in figure 9, where polymer conformation is reduced when polymers enter the entropic barrier between two nanoparticles as observed through experimentation. ^[2]

$$R_g^2 = \frac{Nb^2}{6} = \frac{1}{N} \sum_{i=1}^n (r_i - r_c)^2 \quad (\text{Eq. 5}) \quad [2]$$

Using Eq.5 for R_g the confinement can be investigated through D/D_0 relation against $l_D/2R_g$.

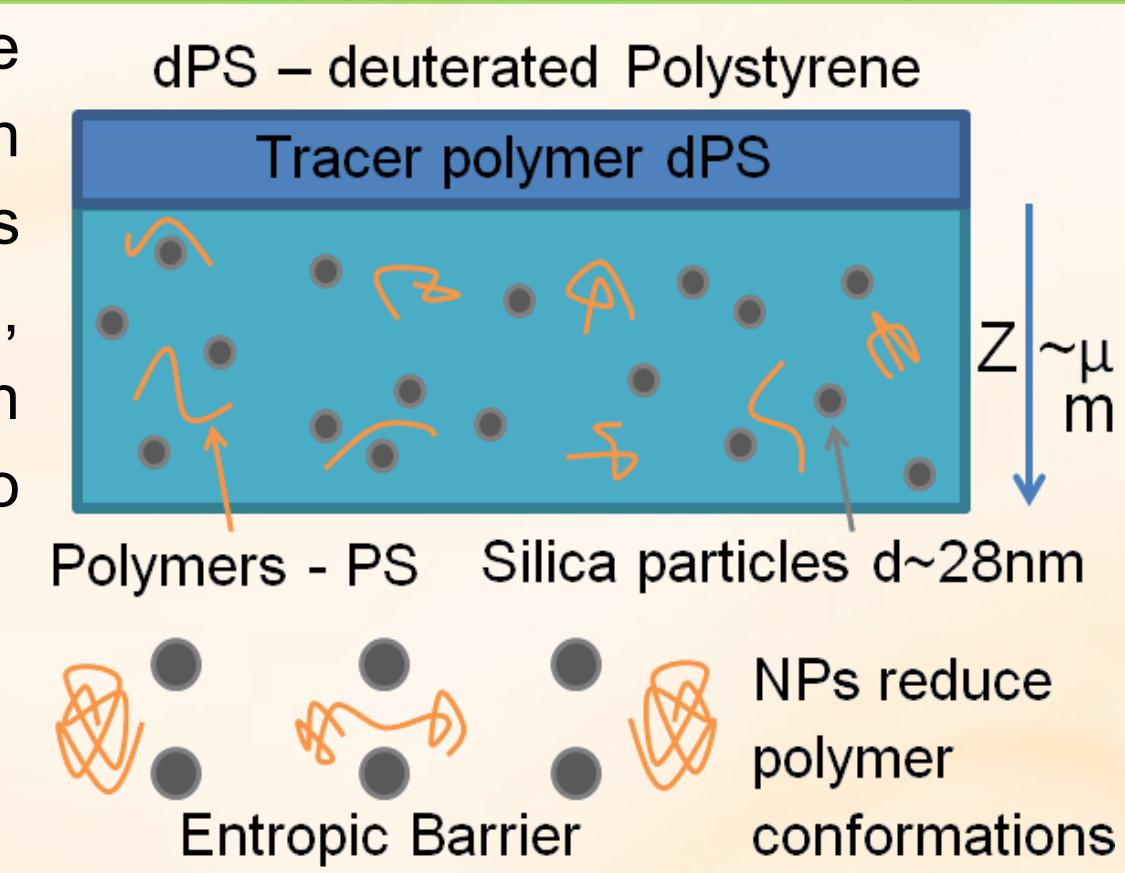


Fig 9. Pictorial representation of experimental PS/DPS polymer & NP setup investigation diffusion

Acknowledgments

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