

# COMMENTS

## Comment on "Local Knot Model of Entangled Polymer Chains"

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In a recent series of papers, Iwata and Tanaka<sup>1</sup> (IT) presented an interesting series of dynamic Monte Carlo simulations and a theoretical analysis of a model system comprised of monodisperse ring polymers restricted to a simple cubic lattice. The model system was constructed in a way that all the rings catenate; i.e., they form a permanent network of mutually knotted and self-knotted chains. The collective motion of the system, particularly the motion of single polymers down their closed contour, has been analyzed. In such a gel-like system, the global self-diffusion mode is shut down due to lack of any mechanism of polymer disentanglement. Consequently, by construction, the only possible long time motion of a probe segment is reptation down a closed path defined by the ring topology, much like a snake chasing its tail. For this system, the authors have estimated various static and dynamic properties<sup>1,2</sup> for rings of various degrees of polymerization.

While the analysis of the properties<sup>1,2</sup> of the IT system is interesting in its own right, the comparison with other simulations is very confusing and contains a number of misleading statements. In particular, they refer to our earlier simulations,<sup>3</sup> which were done at the same volume fraction of lattice polymers. Apparently, they mismatch our estimations of the entanglement length,  $n_e$ , for linear polymers with that for ring polymers. They quoted our  $n_e(\text{linear}) = 133$  as being too small. In reality, our estimation for ring polymers<sup>4,5</sup> with excluded volume is  $n_e(\text{unknotted rings})/n_e(\text{linear}) = 3.9$ . The last estimate gives an  $n_e(\text{rings})$  which is more than 2 times larger than that of Iwata and Tanaka. This is not surprising since our uncatenated (not permanently knotted) rings have mean dimensions smaller than Gaussian, as they should,<sup>4,5</sup> while IT rings were originally prepared as phantom (ideal) chains. The resulting interpenetration of the excluded volume system leads to Gaussian (and *much larger*) dimensions.<sup>1</sup> Therefore, their entanglement length is expected to be much smaller than our estimate for rings. On the other hand, since their rings also experience topological constraints (although they are ill-defined due to their method of chain construction), one would expect their entanglement length to be larger than our linear chain estimate, as has been found.

To avoid further confusion, we compare some numerical results of selected simulations in Table I.

An additional comment is required in response to several statements by IK which suggest that the results of molecular dynamics simulations of a related polymer melt model by Kremer and Grest<sup>6</sup> (KG) contradict our results. As a matter of fact, the numerical results of both studies are in excellent agreement when the same quantities are measured. (See appropriate comments in KG work,<sup>6</sup> and other analyses;<sup>7</sup> some data are also included in Table I.) We disagree with KG only in the conclusion as to whether or not the simulated chains reptate. In reptation, at long times and for long polymers, the collective motion, on average, perpendicular to the local chain axis is strongly suppressed, and consequently the longitudinal motion dominates. KG assume that the  $t^{1/4}$  regime in the single mer autocorrelation function and a self-diffusion coefficient  $D$  scaling as  $n^{-2}$  prove the reptation

TABLE I: Comparison of Some Results of Selected MC and MD Studies of Long Polymeric Chains (Monodisperse Systems)<sup>a</sup>

type of polymer (reference)	$\phi$	$N$	$n$	$n_e$	$D$	scaling relations	
						$g(t)$	$\langle S^2 \rangle$
rings <sup>1</sup> (knotted)	0.5	32	512	230	na	na	$n^1$
rings <sup>3,4</sup> (not knotted)	0.5	40	1536	515	$n^{-1.42}$	$t^{0.41}$	$n^{0.88}$
linear <sup>3</sup> (cubic)	0.5	40	800	120–	$n^{-2}$	$t^{0.28}$	$n^{1.02}$
linear <sup>5</sup> (MD)	$(\rho =$	100	200	35	$n^{-2}$	$t^{0.28}$	$n^1$
	0.85)			133			

<sup>a</sup>  $\phi$  is the volume fraction of the polymer in the lattice models ( $\rho$  is the density with respect to close packing for the continuous model).  $N$  and  $n$  are number of chains and chain length for the largest system studied within the time interval at least in the range of the longest relaxation time.  $n_e$  is the number of chain segments between entanglements.  $D$  is the self-diffusion coefficient.  $g(t)$  is the single mer autocorrelation function (for the central part of the chain).  $\langle S^2 \rangle$  is the mean square radius of gyration of a polymer chain. (In the cases where no decimal point in the exponent is written, the number means the observed asymptotic value.)

model of the chain motion. However, we have shown<sup>3,5</sup> that, in a regime when these scaling behaviors hold, the microscopic picture of chain relaxation obtained by directly monitoring and analyzing the motion of the chain contour (after averaging out the local fluctuations) has nothing whatsoever in common with the reptation picture of a chain slowly sliding out of the tube formed by other chains. Subsequently, KG presented a series of superimposed snapshots of longer chains.<sup>6</sup> These snapshots form a tubelike object, and this was suggested to be proof of reptation. This conclusion is not justified, since the time scale of this particular simulation is many times too short to see any mode of overall relaxation of the chain conformation. Only local fluctuations were probed. We are unaware of any simulations of an unconstrained polymeric system (nongelated) which demonstrate the reptation mode of chain relaxation. While we believe that our simulations of dense systems are probably long enough to argue against the reptation mechanism, much longer polymers are required in order to definitively clarify the microscopic picture of polymer relaxation.

Finally, let us note that the IT studies<sup>1,2</sup> provide a quite detailed picture of motion in a gel-like system, where a kind of reptation mode presumably dominates (a very slow motion of the probes in comparison with other simulations). It is, however, unclear what insights, if any, into the more general problems of the dynamics of uncatenated rings much less that of linear chains emerge from this study. First of all, the systems studied by IT have strikingly differently equilibrium properties from uncatenated rings as well as linear chains. Second, the IT system has a very specific interplay between permanent and temporary knots (with a very collective relaxation of the latter type of constraints) which is absent in any real polymer melt. Finally, as mentioned above, there are a substantial number of misinterpretations and errors in the IT discussion of other works (see ref 5 and references cited therein).

### References and Notes

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