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## Conjectures on the statistics of ring polymers

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**Résumé.** — Dans cet article, nous proposons quelques conjectures sur le comportement statique et dynamique des polymères en anneaux. Lorsque ceux-ci sont non attachés et en phase fondue, ils pourraient avoir un comportement statistique intermédiaire entre ceux de chaînes gaussiennes et de chaînes collapsées. Un traitement très simple (à la Flory) suggère que le rayon  $R$  des anneaux suit une loi de puissance en fonction du degré de polymérisation  $N$  avec l'exposant  $\nu = 2/5$  ( $R \sim N^{2/5}$ ). Au contraire, un anneau dans une phase fondue de longues chaînes linéaires composées de la même espèce chimique devrait être gonflé. De plus, des anneaux d'une espèce (A) peuvent être compatibles avec des chaînes linéaires d'une autre espèce (B), même lorsque les chaînes linéaires A et B sont incompatibles. Le comportement d'anneaux dans un réseau d'obstacles fixes est aussi discuté. Une analyse simple de la dynamique d'un tel anneau indique que sa constante de diffusion  $D$  (dans un espace à 3 dimensions) suit une loi de puissance en fonction du degré de polymérisation  $N$  avec l'exposant  $-2$  ( $D \sim N^{-2}$ ). Cette prédiction est confirmée par des calculs de simulation sur ordinateur. Enfin nous proposons qu'un anneau noué formé irréversiblement dans un solvant  $\theta$  et dans des conditions particulières, doit rester gaussien une fois placé en bon solvant.

**Abstract.** — We present some conjectures concerning the equilibrium statistics and dynamics of ring polymers. We argue that unconcatenated ring polymers in the melt may have statistics intermediate between those of collapsed and Gaussian chains. An extremely crude (Flory-like) treatment suggests that the radius  $R$  of such a ring scales with its polymerization index  $N$  as  $R \sim N^{2/5}$ . In contrast, a ring in a melt of long linear chains (of the same chemical species) should be swollen. Moreover, rings of one chemical species (A) can be compatible with linear chains of another (B), even when linear chains of A and B are not compatible. Rings in a network of fixed obstacles are also discussed. A simple analysis of their dynamics shows that the diffusion constant  $D$  of such a ring (in three dimensions) scales with its polymerization index  $N$  as  $D \sim N^{-2}$ . This prediction is confirmed by computer simulations. Finally, we consider a knotted ring formed irreversibly in a theta solvent, and argue that, under appropriate formation conditions, such a ring may remain Gaussian when placed in a good solvent.

### 1. Introduction.

The equilibrium statistics of flexible, linear chain polymers are by now quite well understood [1]. Relatively little is known, however, about the statistics of « ring polymers ». These are long, flexible-chain polymers which are made (for example) in dilute solution by covalently linking the ends of a linear chain together. It is expected that, under appropriate synthesis conditions, large rings can be made which are neither knotted with themselves, nor concatenated with one another [2] (Fig. 1).

A major reason for the lack of progress in understanding rings is the fact that the configurations of a given ring are restricted to a single topological class. Even in the simplest idealized case of unknot-

ted, unconcatenated rings (to which, with the exception of section 4, we restrict our attention in this paper) it is not obvious how to write down an appropriate partition function. Despite this, a number of theoretical discussions (and some numerical results) [3-8] concerning the statistics of rings at low densities have been given <sup>(1)</sup>. There is also a certain amount of experimental data for chain statistics in the dilute regime [9, 10].

<sup>(1)</sup> Note that most theoretical treatments have considered only the effects of the simplest topological invariant, the winding number, and have avoided analysing the effects of an infinite number of higher topological invariants.

Less seems to be known about the equilibrium statistics of ring polymers at high densities. For example, if the solvent is evaporated off from a dilute solution of ring polymers, one is left with a melt of rings; in such a melt, the rings must remain unconcatenated so long as covalent bonds are not broken. There have been experimental studies of the *dynamics* of polymers in such a melt [11, 12], and of dilute ring polymers in a linear matrix [13]; however, the interpretation of the results remains somewhat controversial [14]. In this speculative paper, we consider the equilibrium statistics of ring polymers in dense systems. To our knowledge, measurements of the gyration radius of such polymers have not been made — possibly because of a widespread assumption that rings, like linear chains at melt densities, obey Gaussian statistics.

We argue here that rings in the melt are very possibly *not Gaussian*. This is because the topological interaction which ensures that two rings always remain unconcatenated is not necessarily « screened out » by the presence of a high density of other rings. (This contrasts with conventional excluded volume interactions, which are fully screened). Similarly the requirement that one ring is not knotted with itself should lead to the swelling of an isolated ring polymer in a melt of linear chains.

## 2. Static configurations.

### 2.1 A RING POLYMER IN A FIXED NETWORK. —

Before considering the effect of topological interactions in melts containing ring polymers, we discuss a simpler case; that of a ring which is free to move in a fixed network (but which is not concatenated with

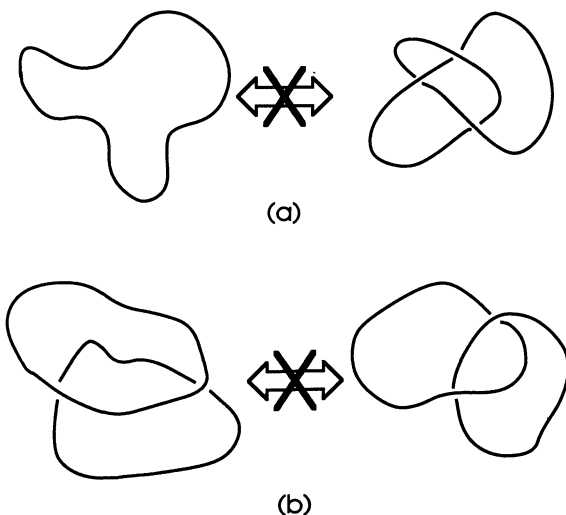


Fig. 1a. — On the left is a permitted configuration of an unknotted ring. It cannot turn into the forbidden (knotted) configuration on the right (nor *vice versa*).

Fig. 1b. — On the left is a permitted configuration of a pair of unknotted, unconcatenated, rings. It cannot turn into the forbidden (concatenated) configuration on the right (nor *vice versa*).

it). For example, one can consider a uniform gel in contact with a reservoir containing a very dilute solution of rings. In this case, since the ring can enclose none of the fixed obstacles, its statistics are those of a branched polymer or « lattice animal » of a tree-like structure [15] (Fig. 2a). Note that this lattice animal is self-avoiding at large length scales, since a fixed network cannot adjust its density so as to screen out the excluded-volume interactions between points on the added ring. (For similar reasons, a linear polymer in a fixed network is a self-avoiding walk (SAW) at large distances [16].) On a scale very much larger than the network of obstacles, the size  $R$  of a ring polymer in a network thus scales with the polymerization index  $N$  as  $R \sim N^\nu$  where

$$\nu = 1/2. \quad (1)$$

This exact result of Parisi and Sourlas [17] for self-avoiding lattice animals in three dimensions is coincidentally the same as for a Gaussian chain or ring; however, all other aspects of this structure are entirely different.

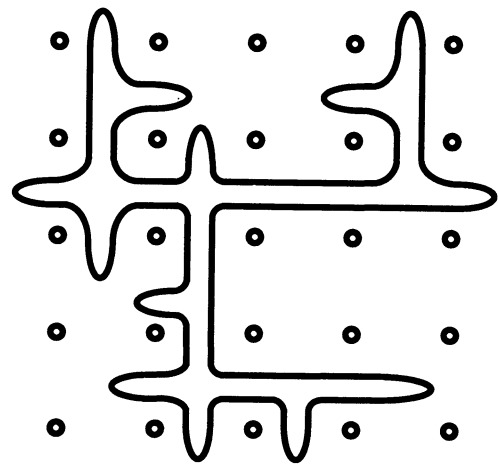


Fig. 2. — A three-like lattice animal corresponding to the structure of a ring in a fixed network. (See also reference [15]).

Thus a ring polymer in a fixed network looks like a self-avoiding lattice animal ( $\nu = 1/2$ ), whereas a linear chain would be an SAW ( $\nu = \nu_{\text{SAW}} \cong 3/5$ ). We see that the topological interaction of the ring with the network leads to a considerable reduction in the size of the ring. Moreover, the entropy of a ring polymer in a fixed network is severely reduced from that of a chemically similar linear chain of the same polymerization index,  $N$ , in an identical network. Specifically, we expect the increase in free energy,  $\Delta F$ , to vary asymptotically as [1, 18, 19]

$$\Delta F/kT \cong AN + O(\log(N)) \quad (2)$$

where  $A$  is a constant. Thus the equilibrium concentration of ring polymers in a gel which is held in

contact with a solution of such rings should be strongly suppressed, compared with a similar experiment using linear chains of the same chemical composition.

**2.2 RINGS IN RINGS.** — We now turn to the more difficult problem of calculating the equilibrium statistics of ring polymers in the melt. Here the obstacles are not fixed, but instead consist of strands of other ring polymers. All configurations of the ring melt are equally likely subject to the constraints that :

(a) no two monomers, whether on the same or different chains, occupy the same spatial position (this is the usual excluded volume interaction) ;

(b) no two rings are concatenated, nor is any ring knotted with itself.

Of these two interactions, the first is completely screened out, so long as each chain remains overlapped with many other chains [1, 18, 20]. Hence the screening of excluded volume is complete even for partially collapsed chains so long as these have  $\nu > 1/3$  in three dimensions. (In two dimensions the requirement is  $\nu > 1/2$ ; thus linear chains in the melt are themselves marginally swollen [1].)

To account for constraint (b) is much more difficult. We first consider two proposals concerning the ring polymer melt and show that neither is fully self-consistent. We then give a crude argument along the lines of Flory [18] which leads to a non-trivial self-consistent estimate for  $\nu$ . (Of course, « self-consistent » does not necessarily mean « correct ».)

The first proposal is to say that in a melt of rings, all the rings are, in fact, Gaussian. Supposing this to be true, let us imagine adding one extra ring to the system. This can be done by first creating a very slight density deficit in some region: this is a « correlation hole » [1] into which we then add the extra ring. There is an immediate problem, however: even at the lowered density, the region in question contains a very large number of rings, which make up a complicated network of strands. We somehow have to add the extra ring in such a way that it is not concatenated with any of these neighbouring rings. In view of this constraint, it seems very implausible that the added ring would be Gaussian. Instead, to avoid threading the other rings it would have to curl up into some more collapsed structure. Thus the assumption of Gaussian rings is not really self-consistent <sup>(2)</sup>.

An opposite approach is to say that for any ring, the topological constraint of nonconcatenation with other rings is so strong that these other rings can be treated as a fixed network for the purposes of topology. Unlike a fixed network, however, the system is certainly able to equilibrate its density, and

<sup>(2)</sup> Of course, there are many ways of forcing the ring to be Gaussian. One way is to insist that the ring doubles back perfectly on itself, forming a linear chain of half the length and twice the thickness of the original ring. However, even in a fixed network, such configurations are extremely unlikely; they carry a probability  $\sim e^{-N}$ .

so screen out excluded volume effects. But in a fixed network, with screened excluded volume interactions, any given ring would be a segregated, collapsed structure of  $\nu = 1/3$ . (This result arises because an ideally Gaussian lattice animal has  $\nu = 1/4$ , which is less than that of a compact structure in 3 dimensions.) Hence this proposal is also not self-consistent: in such a segregated system, each ring overlaps only marginally with its neighbours, and is thus very unlikely to behave as these formed a fixed network of constraints.

In an attempt to obtain a self-consistent theory, we allow the rings (of polymerization index  $N$ ) to have some arbitrary size  $R(N)$ . We then estimate the free energy per ring. If a ring has size  $R$ , it is overlapped with a number of neighbouring rings of order  $R^d/N$  (in  $d$  dimensions). The more spatially extended the ring, the more entropy is lost by the nonconcatenation constraint with its neighbours. The simplest possible estimate of this is to say that roughly one degree of freedom is lost for each of the  $R^d/N$  neighbours which the ring is prevented from threading <sup>(3)</sup>. This gives a contribution to the free energy

$$F \sim kTR^d/N. \tag{3}$$

On the other hand, there is also an entropy penalty if the ring becomes too squashed. Now, the free energy required to squash a Gaussian chain of  $N$  steps into a region of linear size  $R$  less than  $N^{1/2}$  scales as  $kTN/R^2$  [1]. Of course, there are also terms associated with the increased topological entropy loss (from the fact that the ring is not knotted with itself) upon squeezing; we hope these terms are unimportant <sup>(3)</sup>.

Hence we write

$$F(R)/kT \sim R^d/N + N/R^2 \tag{4}$$

which, upon the usual minimization, yields

$$R \sim N^{2/(d+2)} \tag{5}$$

or  $R \sim N^{2/5}$  in three dimensions <sup>(4,5)</sup>.

<sup>(3)</sup> Here we neglect large local contributions to the free energy arising from the exclusion of configurations which are knotted or concatenated at very short length scales. We expect these contributions to be fully screened, i.e., they generate a free energy dependent only on the local density, which is constrained to be everywhere constant.

<sup>(4)</sup> More generally, one might argue that the form (3) for the estimated entropy loss due to the nonconcatenation constraint should be replaced by  $F \sim kT(R^d/N)^a$  where  $a$  is an unknown exponent. This gives, instead of equation 5,

$$R \sim N^{\nu(a)} \quad \text{where} \quad \nu(a) = (a+1)/(da+2).$$

Hence

$$\nu(0) = 1/2 \quad (\text{Gaussian statistics}),$$

$$\nu(\infty) = 1/d \quad (\text{compact statistics}).$$

Some remarks are now in order. Firstly, equations (3)-(5) are to be taken seriously only for  $d = 2$  and  $d = 3$ . For, unlike the case of excluded-volume interactions, it is not clear that topological interactions can be discussed meaningfully in noninteger dimension  $d$ . It should also be noted that for  $d \geq 4$ , there are no knots [21]. Hence the topological interaction between rings does not exist, and the estimate (3) of the constraint energy is inapplicable — instead the rings are Gaussian. For a two-dimensional melt of ring polymers, on the other hand, we obtain  $\nu = 1/2$ . Since this result corresponds to both the Gaussian and the segregated chain limit, it is presumably indeed correct for the melt of rings in two dimensions.

Our second remark is that if one accepts (4) as the free energy, it seems likely that the minimization procedure which follows from it is fairly reliable. This is because each chain is interacting with many others, and fluctuations are small. Thus the usual objections to Flory theories for excluded volume problems [1, 22] do not really arise. Against this should be weighed the fact that our intuition for these topological interactions is not highly developed, and we do not know to what extent mean field arguments apply even at high density. Moreover, we stress that we have not provided any rigorous justification for the terms which appear in equation (4). Therefore we do not attach much significance to the actual value of  $\nu = 2/5$  that was obtained; our motive for presenting the above calculation is only to make more plausible our conjecture that rings in the melt have some value of  $\nu$  intermediate between  $\nu = 1/2$  (Gaussian) and  $\nu = 1/3$  (segregated).

**2.3 RINGS IN LINEAR CHAINS ; RINGS IN SOLUTION.** — For a ring polymer in a melt of linear chains there are no topological constraints other than that the ring always remains unknotted with itself. This constraint on its own is capable of causing the ring to swell. (For example, one expects an isolated ring polymer to be distinctly swollen in a solvent which is at the theta point  $T_\theta$  for a linear chain of the same chemistry [3-7].) The question is whether this topological self-interaction is screened out by the presence of dense linear chains.

Crudely, we can imagine dividing the topological self-interaction of the ring into two parts [6]: a short-range part, and a global part. The short-range part arises because, wherever two sections of the ring are close together in space (Fig. 3), very many local configurations are lost through the topological constraint. (Essentially, one must discard some

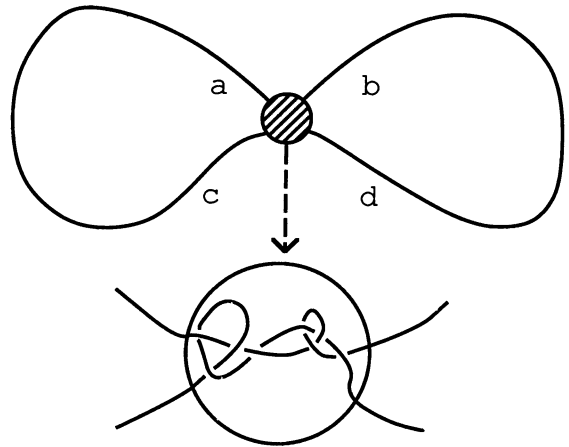


Fig. 3. — Short-range repulsion between points on a ring generated by topological interactions. Knotted configurations, such as that shown, are forbidden.

finite fraction of the configurations in which there is a knot between the points a, b, c, and d<sup>(6)</sup>.)

Following a suggestion of des Cloizeaux [6], we account for this short range part of the topological interaction by setting the excluded-volume interaction between points on the ring to be somewhat larger than between points on other chains (or between one point on the ring and one on another chain). Consequently, a ring and a linear chain of the same chemical species should have a *negative*  $\chi$  parameter<sup>(7)</sup>. This means that a single ring polymer in a melt of linear chains of an identical chemical species should be swollen. Similarly, it may be possible to find pairs of chemical species A, B such that linear chains of each species are incompatible ( $\chi > 0$ ), but that rings of one species are compatible with linear chains of the other ( $\chi < 0$ ). This remark applies even in the limit of very long chains; it would be very interesting to see if this *compatibili-*

<sup>(6)</sup> This assertion rests on the rather plausible assumption that the probability of there being an exactly matching « antiknot » nearby is not very close to unity.

<sup>(7)</sup> For two polymers A, B with excluded volume parameters  $w_{AA}$ ,  $w_{BB}$  and  $w_{AB}$ , the effective interaction  $w$  between points on the A polymer in a melt of chains B obeys [20]

$$w = w_{AA} - w_{AB}^2 / w_{BB}.$$

If A and B are respectively ring and linear polymers of the same chemical species, then  $w_{BB} \equiv w_{AB}$  but  $w_{AA} = w_{BB} + w_t$ , where  $w_t$  is a topological contribution. Hence  $w = w_t$ , and the conformation of the loop A in the melt of linear chains B is the same as it would be in a solvent at the theta temperature  $T_\theta$  of the linear chain. (In such a solvent,  $w_{BB} = 0$ ,  $w_{AA} = w_t$ ). The Flory  $\chi$  parameter is related to the excluded-volume parameters by  $\chi \propto w_{AB} - (w_{AA} + w_{BB})/2 = -w_t/2$ . For a discussion, see reference [1].

All intermediate  $a$  give  $1/d < \nu(a) < 1/2$ . Thus, whilst our choice of  $a = 1$  is the simplest possible, our qualitative conclusions apply for any finite positive  $a$ .

<sup>(5)</sup> The fact that this exponent is greater than  $1/3$  means that excluded volume interactions are fully screened, so that it was consistent not to include them in equation (4).

zing effect of the topological interaction could be detected experimentally.

Under certain conditions, the local excluded volume interaction, including the topological contribution, can be made to vanish. (For example, this will happen for a ring polymer in solution at a shifted theta temperature,  $T_{\theta^*}$ , somewhat below that of the linear chain analogue.) This leaves us with a residual, « global » self-interaction of the ring which comes from the impossibility of configurations like that in figure 1, in which parts of the ring are not in close contact but the ring is globally knotted. Sadly, we do not know how to estimate the strength of this global interaction. Since it is long-range in character, it might in principle turn out to dominate over the local contributions that we have been discussing so far, in the limit of long chains<sup>(8)</sup>. In this case the asymptotic behaviour of a ring in a melt of linear chains (or in a solvent at any temperature  $T > T_{\theta^*}$ ) would be governed by a new exponent  $\nu_{\text{ring}} > \nu_{\text{SAW}}$ . The alternative is that  $\nu_{\text{ring}} = \nu_{\text{SAW}}$  in both of these cases ; this will hold if (as proposed in Ref. [6]) the local part of the topological self-interaction dominates over the global part at high  $N$ .

**3. Dynamics of a ring in a fixed network.**

We now give a discussion of dynamics, concentrating on the case of a ring in a fixed network<sup>(9)</sup> [23]. Here one can estimate the diffusion constant relatively simply, by adapting the « kink-gas » picture of de Gennes [24], as used in the theory of reptating chains. Essentially, diffusion proceeds by the trans-

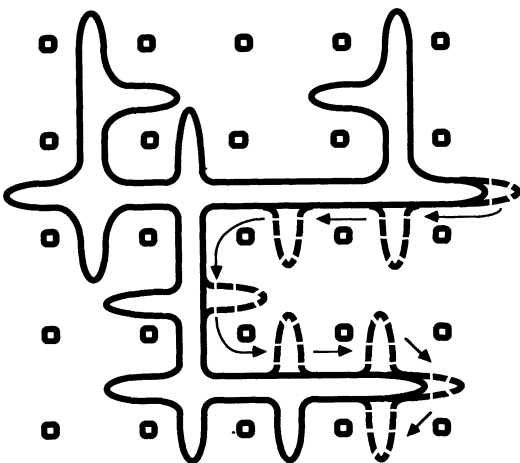


Fig. 4. — Transport of a kink by Rouse-like progression along the chain backbone.

<sup>(8)</sup> For example, if it produced an effective power-law potential between points on the ring.

<sup>(9)</sup> This problem has previously been studied by Rubinstein in reference [23]. However, our results ( $\tau \sim N^3$ ;  $D \sim N^{-2}$  in  $d = 3$ ) are in marked disagreement with his ( $\tau \sim N^2$ ;  $D \sim D^{-9/8}$  in  $d = 3$ ).

port of kinks along the chain (Fig. 4). Each kink takes a time  $\tau_{\text{Rouse}} \sim N^2$  to travel a spatial distance of order  $R(N)$ , the linear size of the polymer. If there were only one kink on the chain at any time, the centre of mass diffusion constant  $D_0$  would obey

$$D_0 \tau_{\text{Rouse}} = R(N)^2 / N^2 \tag{6}$$

where the right hand side represents the mean square displacement of the centre of mass arising from the transport of one kink across a distance  $R$ . In reality, the number of microscopic kinks present at any time is proportional to  $N$ . Hence the true centre of mass diffusion constant  $D$  scales as

$$D \sim ND_0 \sim R(N)^2 / N^3 \sim N^{2\nu(d) - 3}. \tag{7}$$

Here  $\nu(d)$  is the size exponent for self-avoiding animals in  $d$  dimensions. (This obeys  $\nu(d) \cong 5 / (2d + 4)$  [25]; hence  $\nu(2) \cong 5/8$ , whereas  $\nu(3) = 1/2$ , exactly [17], as mentioned in section 2.1.)

It thus appears that (i) the fundamental relaxation time for the centre of mass diffusion of a ring polymer in a fixed network is  $\tau \sim N^3$ , which is the same as the reptation time  $\tau_{\text{rep}}$  for a comparable linear chain in a melt ; (ii) in three dimensions, the diffusion constant  $D \sim N^{-2}$  also scales the same way as for a reptating linear chain. This latter result arises purely from the accidental coincidence of  $\nu$  for Gaussian chains and self-avoiding animals in three dimensions. In two dimensions, one expects  $D \sim N^{-7/4}$ .

We have tested these predictions numerically in both two and three dimensions, with a dynamic Monte Carlo simulation. We used a lattice model similar to that of Evans and Edwards [26], with the addition of a repulsive interaction between chain monomers. We refer the reader to reference [26] for a detailed description of the model. In essence, a ring polymer is placed on a simple cubic lattice ; its motion is restricted by the presence of a « cage » composed of lines that run parallel to the three lattice directions (with one cage line running through the centre of every face of each unit cell). Thus we prohibit the movement of monomers along diagonals, but allow sections that immediately double back on themselves to « flip ». Throughout the motion, the ring remains unconcatenated with the cage. To maintain swollen chain statistics (as discussed in section 2.1) a local two-body repulsion is introduced. The total energy takes the form

$$E = \sum_{i < j} v(r_i - r_j)$$

where  $r_i$  is the co-ordinate of the  $i$ th monomer, and  $v(r) = u$  if  $r = 0$ ,  $v(r) = 0$  if  $r \neq 0$ .

Two dynamical correlation functions were monitored : the mean square displacement of a monomer from its position at time zero, and the mean square displacement of the centre of mass. More speci-

fically, the monomer-monomer displacement  $\langle r^2(t) \rangle$  is defined as

$$\langle r^2(t) \rangle = N^{-1} \sum_{i=1}^N \langle (r_i(t) - r_i(0))^2 \rangle \quad (8)$$

where  $r_i(t)$  is the position of the  $i$ th monomer on the chain at time  $t$ . The average denoted by angle brackets was taken over enough independent runs to obtain adequate statistics.

The centre-of-mass correlation function  $\langle R_{\text{cm}}^2(t) \rangle$  is defined as

$$\langle R_{\text{cm}}^2(t) \rangle = \langle (r_{\text{cm}}(t) - r_{\text{cm}}(0))^2 \rangle \quad (9)$$

where

$$r_{\text{cm}}(t) = N^{-1} \sum_{i=1}^N r_i(t). \quad (10)$$

After initially equilibrating the ring polymer, these correlation functions were computed. The results are displayed in figures 5 and 6.

Theoretically, we may adapt standard arguments, from the theory of reptating polymers [24, 26], to predict that the above correlation functions will have the following behaviour. For  $t < N^2$ , we expect Rouse-like motion occurring on a convoluted path of fractal dimension  $d_t = 1/\nu$ , so that

$$\langle r^2(t) \rangle \cong t^{\nu/2}. \quad (11)$$

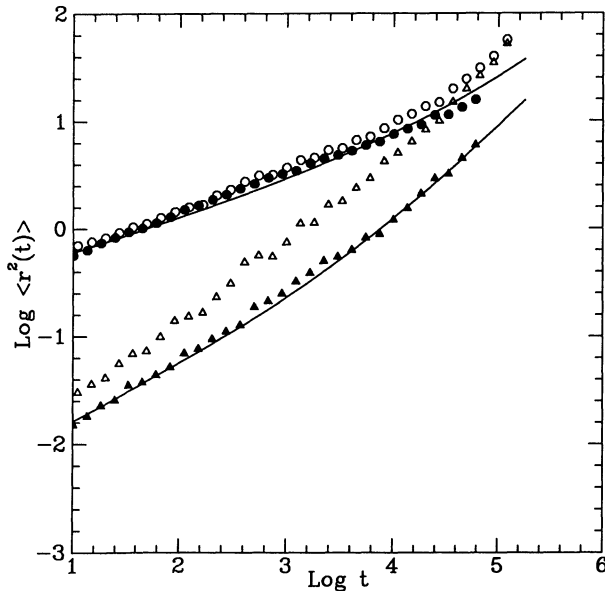


Fig. 5. — Simulations of a swollen ring polymer in a fixed network in three dimensions. The energy penalty for self-intersections is  $U = 0.5 kT$ . The filled circles and triangles denote data points for  $\langle r^2(t) \rangle$  and  $\langle R_{\text{cm}}^2(t) \rangle$  respectively for a ring of length  $N = 60$ . The solid lines are a theoretical fit to this data (described in the text). Open symbols denote corresponding data for a chain of length  $N = 30$ .

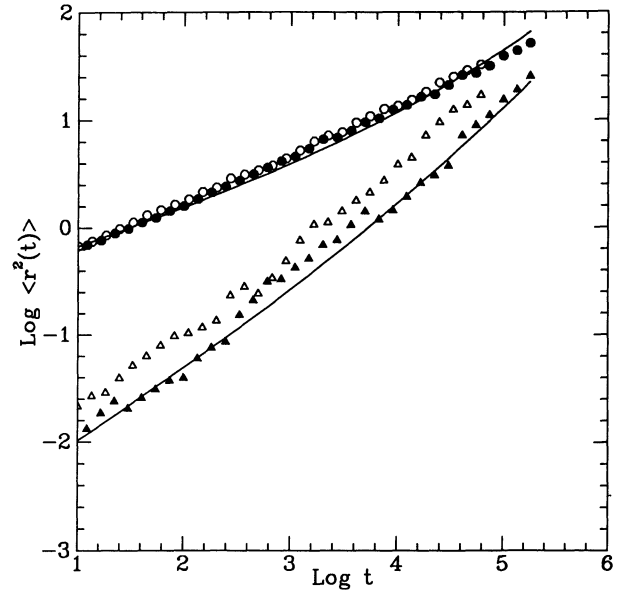


Fig. 6. — Simulations of a swollen ring polymer in a fixed network in two dimensions. The filled circles and triangles denote data points for  $\langle r^2(t) \rangle$  and  $\langle R_{\text{cm}}^2(t) \rangle$  respectively for a ring of length  $N = 90$ . The solid lines are a theoretical fit to this data (described in the text). Open symbols denote corresponding quantities for a chain of length  $N = 60$ .

For  $N^2 < t < N^3$  we expect diffusive motion along the same fractal path. Hence

$$\langle r^2(t) \rangle \sim (t/N)^\nu. \quad (12)$$

The  $N$ -dependence in (12) is obtained by requiring continuity of equations (11) and (12) at  $t = N^2$ . Finally, for  $t > N^3$  we expect normal diffusive motion

$$\langle r^2 \rangle \sim Dt \quad (13)$$

where similar requirements of continuity demand  $D \sim N^{2\nu(d)-3}$  (cf. Eq. (7)).

For the centre of mass motion, we expect

$$\langle R_{\text{cm}}^2 \rangle \sim N^{-1} t^\nu \quad (14)$$

for  $t < N^2$  and

$$\langle R_{\text{cm}}^2 \rangle \sim Dt \quad (15)$$

at longer times. Throughout equations (11)-(14), the relevant  $\nu$  is that for swollen lattice animals ( $\nu = 1/2$  in three dimensions,  $\nu \cong 5/8$  in two dimensions), as discussed previously.

Figure 5 shows simulation data in three dimensions. Motivated by the above arguments, we have fitted the data (for a chain of length  $N = 60$ ) with the functions  $\langle r^2(t) \rangle = 0.000075 t + 0.044 t^{1/2} + 0.26 t^{1/4}$  and  $\langle R_{\text{cm}}^2(t) \rangle = 0.000075 + 0.0049 t^{1/2}$ . In figure 6, simulation results for two dimensions are plotted. The solid curve represents a fit to the

data (for a chain of length  $N = 90$ ) with the functions  $\langle r^2(t) \rangle = 0.001 t + 0.018 t^\nu + 0.29 t^{\nu/2}$  and  $\langle R_{cm}^2 \rangle = 0.001 t + 0.0022 t^\nu$ , with  $\nu = 5/8$ . As can be seen, both sets of data are fitted reasonably well in this fashion. We conclude that these computer simulations are basically consistent with the discussion of dynamics given above, including the result (7).

In contrast, to the above results for a ring polymer in a fixed network, the dynamics of a ring in a melt of other rings could be remarkably complicated. If our conjectures concerning the equilibrium statistics are correct, we expect the dynamics to be slowed down considerably as a result of the interpenetration which neighbouring rings. For a discussion of dynamics in the remaining case of interest — a ring in a linear chain matrix — we refer the reader to a recent article by Klein [27].

#### 4. Knotted rings.

Throughout sections 1-3, we have considered only the idealized limit in which our ring polymers are formed in an unknotted configuration. This limit may be realized experimentally if the rings are made by a polymerization mechanism in which monomers are added one-by-one into a pre-existing unknotted loop. Commonly, however, ring polymers are made by chemically bonding the ends of a long linear chain. This may lead to the trapping of many knots on the ring. One would expect the distribution of knots to depend on the preparation conditions [10]: for example a ring formed in a good solvent should have fewer knots than one formed in a theta solvent or poor solvent.

An interesting limiting case arises if dilute Gaussian chains (in a theta solvent) are made to form loops by the following two-stage process<sup>(10)</sup>: (i) functional end-groups, having a strong but *reversible* dimerization tendency, are incorporated at both ends of each chain; (ii) after a (long) equilibration period, a quenching agent is added which prevents the dimerized end-groups of each chain from coming apart at any later time.

After stage (i) one has an ensemble of « Gaussian rings », i.e., a set of isolated ring polymers with an equilibrium distribution of topologies (these will obey  $R \sim N^{1/2}$ , as usual). After stage (ii), the distribution of topologies is « frozen in ». The quenching procedure should have no effect on the size of the chains at later times (since the quenched sample is unbiased), so long as they remain in a theta solvent.

We now ask, what happens to this ensemble of knotted rings when we put them in a good solvent?

An appealing conjecture is that the rings *remain Gaussian*. For, as discussed in section 2.3, there is (after the quench) a topological two-body repulsion between any two sections of each ring. Hence, upon going to a good solvent, the total two-body repulsion is merely increased from an already positive value. One expects such a change to represent an irrelevant perturbation, i.e., to lead to no change in the exponent  $\nu$  from its Gaussian ring value ( $\nu = 1/2$ )<sup>(11)</sup>. Thus we can argue that an ensemble of knotted rings made by the two stage process in a theta solvent, and then transferred to a good solvent, should have  $\nu = 1/2$ . This would be very different from an ensemble of rings made directly in the good solvent (by an otherwise identical two-stage process). In the latter case, one expects to generate a set of self-avoiding rings, with quenched but unbiased topologies; these would have  $\nu = \nu_{SAW}$ .

#### 5. Conclusions.

In this paper, we have tried to convince the reader that the topological interactions of ring polymers may give rise to qualitatively new effects in systems at high density. For example:

(i) Ring polymers in the melt may be partially collapsed, rather than Gaussian, with an exponent  $\nu$  of about 2/5.

(ii) A single ring polymer in a melt of linear chains, of the same chemical species, should be swollen ( $\nu \geq \nu_{SAW}$ ).

(iii) The topological repulsion between rings may cause an increase in the compatibility of ring polymers of one chemical species and linear chains of another.

(iv) The equilibrium concentration of ring polymers in a gel should be less than that of linear polymers of the same chemical species.

(v) Under certain conditions, rings prepared in a theta solvent may remain Gaussian when placed in a good solvent.

We believe that a more detailed study of the equilibrium statistics of ring polymers in these dense systems, by experiment, theory and computer simulation would be worthwhile. For example, an improved knowledge of the static configurations might make it easier to explain the results of recent experiments [11-14] on the dynamics of these systems. In the case of a ring in a fixed network, the relevant dynamics appear to be simple; the fundamental relaxation time scales like the reptation time for the corresponding linear chain. For the other systems we have discussed, especially for rings in the melt, the dynamics may be much more complicated.

<sup>(10)</sup> The idealized two-stage process described here should be equivalent to a number of other mechanisms by which ring polymers could realistically be made in a Theta solvent. The only requirement is that the set of trapped topologies provide an unbiased sampling of the Gaussian loop ensemble.

<sup>(11)</sup> This argument is not altered when the long range part of the topological interaction is taken into account. For if this interaction dominates the asymptotic behaviour, it is all the more likely that an increase in the local two-body repulsion, from an already positive value, is irrelevant.



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