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Submitted on 1 Jan 1990

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Molecular dynamics simulations of the structure of gelation/percolation clusters and random tethered membranes

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(Reçu le 28 décembre 1989, accepté sous forme définitive le 28 février 1990)

Abstract. — We study the equilibrium structure of isolated (diluted) three dimensional percolation clusters and site-diluted tethered membranes using a molecular dynamics simulation. We find that the percolation clusters swell upon dilution and the fractal dimension changes from 2.5 to about 2, in agreement with recent Flory-type theories and neutron scattering experiments on gelation clusters. The equilibrium configuration of the site-diluted membranes is found to be rough on small length scales but flat asymptotically. We measure the ratio $\phi = \lambda_3/\lambda_0$ where $\lambda_3$ is the largest eigenvalue of the interia matrix at equilibrium and $\lambda_0$ is its value when the membrane is perfectly flat. We find that $\phi$ decreases linearly with decreasing $p$, the fraction of sites present in the membrane. The membranes are shown to have anisotropic scattering functions. Only when $p \rightarrow p_c^+$, where $p_c$ is the percolation threshold, do the membranes become isotropic, indicating that random site-dilution is not sufficient to produce a crumpling of two-dimensional membranes.

1. Introduction.

In 1984, Cates [1] introduced the term « polymeric fractal » to describe the class of fractals which are made of flexible polymer chains at short length scales but have an arbitrary self-similar connectivity at large distances. Examples of such fractal are ordinary, linear polymers, branched polymers and swollen gelation/percolation clusters generated near the percolation threshold $p_c$. Such fractals are interesting because they have no inherent rigidity. Because such systems are locally very flexible, after they are allowed to relax and take on their equilibrium shape, they very often have a very different fractal dimension than they had when they were first constructed. Cates [1] worked out a Flory-level theory [2] in the presence of excluded volume interactions to determine an estimate for the fractal dimension $d_f$ which relates the mass or number of monomers $N$ of the fractal to the size $R_q$, $R_q^{d_f} \sim N$. By balancing the elastic (entropic) free energy of the « phantom » object without self-avoidance with the mean field estimate of the excluded volume interaction, he showed that $d_f$ depends only on the spectral dimension $[3] \tilde{d}$ and the dimension of space $d$

$$d_f = \frac{(d + 2) \tilde{d}}{d + 2}. \quad (1)$$
This is a very important relation since it predicts that $d_f$ is independent of the spatial configuration of the object and depends only on its connectivity.

Despite the fact that the Flory argument is only a simple mean field theory it is known to work very well for a number of cases, often producing estimates for $d_f$ which differ from the exact result by only a few percent or less. One familiar example is that of linear polymers, for which $\tilde{d} = 1$. Flory [2] first worked out this case and found that $\nu = 1/d_f = 3/5$. This result is very close to the best renormalization group estimates [4] which give $\nu = 0.588$. Percolation clusters at the percolation threshold $p_c$ are also good examples of polymeric fractals. Since $\tilde{d} = 4/3$ in all dimensions [3, 5, 6] equation (1) predicts that a single, isolated percolation cluster has a fractal dimension $d_f = 2(d + 2)/5$, independent of the dimension in which it was generated. Thus a percolation cluster made of flexible segments with two dimensional connectivity embedded in 3 dimensions is expected to have the same fractal dimension as a percolation cluster with three dimensional connectivity, namely $d_f = 2$. This result was also found by Daoud et al. [7] who studied the properties of gelation clusters generated just below the sol-gel transition. They showed that gelation clusters swell after the excluded volume interactions from the nearby clusters are screened (removed) and their the fractal dimension which initially was 2.5 in three dimensions is reduced to 2. This swelling is produced by the excluded volume which builds up for intra cluster interactions after the other clusters are removed, exactly as occurs for linear polymers. Their arguments were identical to Cates’ though they did not present their results in terms of the spectral dimension $\tilde{d}$. Gelation and percolation clusters are believed to be in the same universality class [8]. Adam et al. [9], using light scattering, found that the undiluted gelation clusters have $d_f = 2.5 \pm 0.09$ while Bouchaud et al. [10] have verified using small angle neutron scattering that the diluted clusters just below the sol-gel transition have $d_f = 1.98 \pm 0.03$. In this paper we present the first detailed numerical simulations for diluted percolation clusters with either two or three dimensional connectivity embedded in 3 dimensions and show that $d_f$ is indeed 2 within our numerical resolution. Thus we find in agreement with the neutron scattering results [10] that if there are deviations from Flory theory, they are very small.

Another example of a structure which is not a polymeric fractal but for which equation (1) was believed to hold is that of a tethered, self-avoiding membranes in which the monomers are connected to form a regular $D$ dimensional array embedded in $d$ dimensions. Kantor et al. [11-13] have recently analyzed these structures using a variety of techniques including Flory theory, renormalization group calculations and Monte Carlo simulations. It turned out that the Flory theory is identical to that discussed by Cates [1] provided one substitutes $\tilde{d} = D$ in equation (1). For $D = 2$ and $d = 3$, the case most often studied, this theory predicts that $d_f = 2.5$, in which case the membrane would be crumpled. The fact that membranes should crumple is supported by renormalization group calculations [11, 12, 14, 15] and is consistent with the early Monte Carlo simulations by Kantor et al. [11, 12] on small systems. However recent more detailed simulations on larger systems by Plischke and Boal [16], Abraham et al. [17] and Ho and Baumgârtner [18] indicate that these tethered membranes do not crumple. Two of these groups [16, 17] examined the shape of their tethered membranes by studying the eigenvalues of the inertia tensor. They found that they have the scaling behavior $\lambda_1 \sim L^{2 \nu_1}$ and $\lambda_3 \sim L^{2 \nu_3}$, where $\lambda_1$ and $\lambda_3$ are the smallest and largest eigenvalues, respectively. These exponents were found to be consistent with $\nu_3 = 1$ and $\nu_1 = 0.7$, corresponding to a rough but asymptotically flat object.

To obtain a somewhat better insight into why these model topological 2-dimensional tethered membranes do not satisfy equation (1) while polymeric fractals do, it is instructive to consider how the tethered membranes which have been studied numerically to date have been
constructed. In the Monte Carlo simulations of Kantor et al. [11, 12] and Plischke and Boal [16] and the molecular dynamics simulations of Abraham et al. [17], a triangular array of monomers was considered in which all the nearest neighbors are tethered. Ho and Baumgärtner [18] considered two models. The first is similar to that in references [11, 17] except that it has a square lattice topology while the second is for a triangular array of infinitely thin, flexible bonds in which the length of the tethers are limited within 1 and \( \sqrt{3} \). The latter simulation is carried out using a Monte Carlo method in which bead displacements are accepted only if no crossing of bonds occurs, thus providing a model for an impenetrable surface. In all of these cases, the motion of a single monomer is highly constrained since it is connected to four or six nearest neighbors. This high connectivity apparently gives rise to some type of local bending which suppresses the crumpling transition.

While this is one way to produce a tethered membrane, another way one could imagine is a network of crosslinks which is topologically 2-dimensional but which is made up of long flexible linear polymers between the crosslinks. Such a structure would still satisfy the conditions of self-avoidance and have \( D = 2 \), yet be closer to Cates' polymeric fractal. Obviously such an object could be very flexible locally. Whether it would crumple for system sizes much larger than the length of the polymer segments between crosslinks is an open question which remains to be answered. Work in this direction is presently underway by Abraham and Nelson [19]. Another possible way to introduce a local flexibility into the original highly connected membranes is simply to remove some of the monomers randomly. As the fraction \( p \) of monomers present decreases, the average coordination number will decrease. The question that arises then is whether the membrane will crumple before it falls apart at \( p_c \) or simply roughens slightly but remain flat. In this paper, we show that at least for a site diluted triangular lattice, the membrane remains asymptotically flat for all \( p > p_c \). At \( p_c \), there appears to be a discontinuous transition from a flat, highly anisotropic object to an isotropic one. However, as discussed above since diluted percolation clusters have \( d_f = 2 \) in \( d = 3 \) within Flory theory, we have the curious result that the fractal dimension does not change even though the character of the membrane changes considerably at \( p_c \).

While tethered membranes in the presence of excluded volume interactions are not yet very well understood, « phantom » membranes in which the excluded volume interaction is neglected are. In this case one can use a Gaussian approximation [1, 2, 13] and one finds that the fractal dimension \( d_f \) depends only on the object's connectivity through its spectral dimension \( \tilde{d} \),

\[
d_{fo} = \frac{2}{2 - \tilde{d}}.
\]

Here the subscript \( o \) indicates that the excluded volume interaction is absent. This equation reproduces the well-known result for Gaussian linear polymers, namely \( d_{fo} = 1/\nu_o = 2 \). Duering and Kantor [20] found that it also works very well for Sierpenski gaskets. For percolation clusters, if we assume \( \tilde{d} = 4/3 \), equation (2) gives \( d_{fo} = 4 \). In this paper, we confirm this result for topologically 2 and 3 dimensional percolation clusters. For tethered membranes with \( D = \tilde{d} = 2 \), \( d_{fo} = \infty \). A more detailed analysis by Kantor et al. [11, 12] showed that in fact

\[
R_{g0} \sim 1/2 \ln L.
\]

This logarithmic behavior has been confirmed by Kantor et al. [11, 12] using Monte Carlo simulations.

In this paper we examine the properties of percolation clusters generated in both 2 and 3 dimensions and embedded in three dimensions as examples of polymeric fractals and random
tethered membranes using a molecular dynamics simulations in which the monomers are weakly coupled to a heat bath. This method has been very successful in studying the static and dynamic properties of linear polymers [21, 22], star polymers [23] and the interaction between grafted polymeric brushes [24, 25]. In agreement with the Flory theory and earlier neutron scattering experiments for gelation clusters we find $d_f \approx 2$ in the presence of excluded volume interactions. With no excluded volume interaction we find $d_f = 4$. We also studied a number of 2 dimensional random tethered membranes. With no dilution, $p = 1$, we studied systems of size $3 \leq L \leq 55$ on a triangular lattice and find in agreement with earlier studies [17] that the membranes are rough but flat and that $\nu_3 = 1$ and $\nu_1 = 0.7$. For $p < 1$, we could not do finite size scaling in the same way on usually does for $p = 1$. The difficulty is that to produce reliable results for the radius of gyration and the 3 eigenvalues of the inertia tensor for each size $L$ for random membranes, we would need many realizations. However, since the equilibration times for these membranes are very long, of order several million time steps for $N$ of order a few thousand, we are not able to study more than a few realizations for each $p$. Instead, we made several very large membranes, $N$ from 1 to 3 thousand and ran each for of order $3-6 \times 10^6$ time steps. Then to determine the fractal dimension, we measured both the spherically averaged structure factor, $S(q)$, as well as the anisotropic structure factor first defined by Plischke and Boal [16]. In the scaling regime, $S(q) \sim q^{-d_f}$. Thus by varying $q$, we can study the properties of a few membranes on all length scales. We find that as $p$ decreases, our site diluted membranes roughen but do not crumple before falling apart at $p_c$. Following Kantor and Nelson [26], we measured the order parameter defined as the ratio of the largest eigenvalue of the inertia tensor $\lambda_3$ to its value in the initial flat configuration $\lambda_3^0$:

$$\phi = \frac{\lambda_3}{\lambda_3^0}. \quad (4)$$

We find that $\phi$ decreases approximately linearly as $p$ decreases and reaches a value of about 0.31 at $p_c^+$. Then $\phi$ must drop discontinously to zero. Thus the introduction of randomness, in this case site dilution, does in fact reduce $\phi$ but not all the way to zero which is the necessary condition for the membrane to be crumpled. Though these results are encouraging, if one would like to find a crumpled membrane, it does not appear that random site dilution alone is insufficient to produce the desired results. Possibly some combination of random and/or correlated disorder [19] will cause the membranes to crumple, but this remains to be seen.

In section 2, we describe the model and the molecular dynamics technique used to perform the simulations. Because we are using a molecular dynamics instead of a Monte Carlo method, the potential between the monomers is continuous. It differs in its detail from that chosen by Abraham et al. [17]. In section 3, we present our results for percolation clusters, while in section 4, we describe our results for site diluted tethered membranes. Finally in section 5, we briefly summarize our results and indicate some future directions.

2. Model and method.

The equilibration of the polymeric membranes is achieved using a molecular dynamics method [21] in which each monomer is coupled to a heat bath. Each membrane consists of $N$ monomers of mass $m$ connected by anharmonic springs. The monomers interact through a shifted Lennard-Jones potential given by

$$U^0(r) = \begin{cases} 4 \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right] & \text{if } r \leq r_c; \\ 0 & \text{if } r > r_c, \end{cases} \quad (5)$$
with \( r_c = 2^{1/6} \sigma \). This purely repulsive potential represents the excluded volume interactions that are dominant in the case of monomers immersed in a good solvent. For monomers which are tethered (nearest neighbors) there is an additional attractive interaction potential of the form [27]

\[
U^{\text{bond}}(r) = \begin{cases} 
-0.5 \ k R_0^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] & \text{if } r \leq R_0; \\
\infty & \text{if } r > R_0.
\end{cases}
\]

The parameters \( k = 30 \ \epsilon / \sigma^2 \) and \( R_0 = 1.5 \ \sigma \) are chosen to be the same as in reference [21]. Note that the form of the potential is somewhat different from those used by Kantor et al. [11, 12], Plischke and Boal [16] and Abraham et al. [17] in that there exists no range of separation \( r \) in which the force vanishes. Also note that this potential does not include any explicit bending terms.

Denoting the total potential of monomer \( i \) by \( U_i \), the equation of motion for monomer \( i \) is given by

\[
m \frac{d^2 r_i}{dt^2} = -\nabla U_i - m \Gamma \frac{dr_i}{dt} + W_i(t).
\]

Here \( \Gamma \) is the bead friction which acts to couple the monomers to the heat bath. \( W_i(t) \) describes the random force acting on each bead. It can be written as a Gaussian white noise with

\[
\langle W_i(t) \cdot W_j(t') \rangle = \delta_{ij} \delta (t - t') 6 \ k_B \ T \Gamma,
\]

where \( T \) is the temperature and \( k_B \) is the Boltzmann constant. We have used \( \Gamma = 0.5 - 1.5 \ \tau^{-1} \) and \( k_B T = 1.0 \ \epsilon \). The equations of motion are then solved using a fifth-order predictor-corrector algorithm [28] with a time step \( \Delta t = 0.006 \ \tau \). Here \( \tau = \sigma (m / \epsilon)^{1/2} \).

The program was vectorized for a Cray supercomputer following the procedure described by Grest et al. [29] except that the periodic boundary conditions were removed and additional interactions between monomers which are tethered are added. The cpu time per step increased approximately linearly with \( N \). For the three dimensional percolation cluster with \( N = 3 \ 966 \), the program took about 17 hours of cpu time for \( 10^6 \) time steps with excluded volume interactions and 12 hours without. With this choice of parameters, the average bond length between nearest neighbors that are tethered is found to be 0.97 \( \sigma \). The maximum extension of the bonds are monitored during the course of the simulation in order to assure that no bond-crossing occurred. Further details of the method can be found elsewhere [21].

We simulated systems whose initial configurations were that of a three dimensional percolation cluster very near the percolation threshold, \( \rho_c \) as well as two dimensional clusters for a range of \( \rho > \rho_c \). The 3d clusters were generated on a simple cubic lattice with open boundary conditions by diluting the lattice down to a density of \( \rho = 0.33 \), slightly above the percolation threshold [30] of \( \rho_c = 0.31 \). We preferred not to simulate systems exactly at \( \rho_c \) as those systems would have very non-representative structures. The sizes of the systems that we simulate at \( \rho = 0.33 \) are still smaller than the correlation length at the same \( \rho \). We then eliminated all the clusters except for the largest one. The clusters, which were subsequently equilibrated and studied in detailed, were of size \( N = 622, 856, 980, 1 \ 136 \) and 3 966. Typically 1-3 million time steps were needed to equilibrate the clusters. After equilibration, the simulations were run for an additional \( 4 \times 10^6 \) steps, during which the desired quantities were averaged. The initial configurations for the topologically planar
objects were constructed on a triangular lattice. A section in the form of a hexagon \([16, 17]\) with sides of length \(L\) was diluted to an occupation fraction \(p\), with \(p > p_c = 0.5\). Again, all but the largest cluster were eliminated. The number of monomers, \(N\) and the lattice size, \(L\) for the cases that were simulated are shown in table I. Also shown in the table are the total duration of the runs (after equilibration) in units of \(\tau\), the eigenvalues of the inertia matrix of the equilibrated membranes and \(\phi\). Typically 1.0-2.5 million steps were needed to equilibrate the systems. The equilibration of all the systems was checked by monitoring the autocorrelation function of the radius of gyration of the membranes.

We also performed simulations of initially planar undiluted membranes (\(p = 1\)) for a range of \(L\) values, \(13 \leq L \leq 55\). For these membranes, the number of sites, \(N\), is given by \(N = (3L^2 + 1)/4\). The simulations were run for \(1-6 \times 10^6\) time steps after equilibration. Finite size scaling analysis for the moments of inertia tensor agree with Abrahams et al.'s results that \(\nu_3 = 1.0\) and \(\nu_1 = 0.7\).

Percolation clusters at \(p = p_c\) with no excluded volume interactions were also studied. This was done by simply eliminating the Lennard-Jones repulsion between all monomers which were not tethered. The interaction between the tethered monomers remained equal to the sum of the Lennard-Jones potential, equation (5) and the anharmonic spring, equation (6). The bond length between tethered monomers remained the same as in the excluded volume case. Equilibration of these membranes required much longer runs (up to \(4 \times 10^6\) time steps), as the starting states for these membranes were far away from equilibrium.

To analyze our results were calculated several quantities. Typically every 100 steps we calculated the inertia matrix, its eigenvalues \(\lambda_i (\lambda_1 < \lambda_2 < \lambda_3)\) and the radius of gyration squared, \(R_g^2\), given by their sum. These quantities were also used to check the equilibration of the system through their autocorrelation. The spherically averaged structure factor, \(S(q)\), given by

\[
S(q) = \frac{1}{N} \left\langle \sum_{i,j} e^{iq \cdot (r_i - r_j)} \right\rangle,
\]

Table I. — The occupation probability, \(p\), lattice size, \(L\), the number of monomers in the cluster, \(N\) and the total duration of the run after equilibration, \(T_r/\tau\), in units of \(\tau\), for the topologically planar objects simulated with excluded volume interactions. Also shown are the average values of the three eigenvalues of the inertia matrix of the equilibrated membranes and order parameter \(\phi\), equation (4) for \(p \geq 0.6\).
we also calculated. The angle brackets represent a configurational average typically taken every 1000 time steps in the present simulation. For each \( q = |q| \), we averaged over 20 random orientations. In the scaling regime, \( S(q) \sim q^{-d_f} \). Following Plischke and Boal [16], we also considered the anisotropic scattering intensity, \( S_i(q) \), where the \( q \)'s were restricted to be parallel to the eigenvector \( \hat{e}_i \) of the inertia matrix corresponding to the eigenvalue \( \lambda_i \). Since the topologically planar membranes with \( p > p_c \) turned out to have \( \lambda_3 = \lambda_2 \gg \lambda_1 \), instead of simply measuring \( S_2(q) \) and \( S_3(q) \) separately, we calculated

\[
S_\perp(q) = \frac{1}{N} \left\langle \sum_{i,j} e^{i|q| \cdot (r_i - r_j)} \right\rangle,
\]

such that \( q_\perp \) is perpendicular to \( \hat{e}_1 \). We averaged over 40 random orientations of \( q_\perp \) for each \( q = |q_\perp| \). If in the future it becomes possible to produce tethered membranes in the laboratory, then presumably one will also be able to orientate them into lamella similar to what has been done for fluid membranes [31]. In this case the experimentally measurable anisotropic scattering intensities are those with \( q \)'s parallel to \( \hat{e}_1 \) and perpendicular to it, i.e. \( S_1(q) \) and \( S_\perp(q) \). As will be shown in the next two sections, these anisotropic scattering functions were very useful in demonstrating that for \( p > p_c \), the tethered membranes were anisotropic and not crumpled, while those close to \( p_c \) were isotropic.

3. Dimensional percolation clusters.

Figure 1 shows the initial configuration of the 3d percolation cluster at \( p = 0.33 \) with \( N = 3966 \) particles and a snapshot of the same cluster after \( 6.5 \times 10^6 \) time steps. The linear dimensions of the cluster have increased considerably after the relaxation and it has a more open structure. In order to quantify the change in the structure of the cluster, we show in

\[
\begin{align*}
\text{a) } & t = 0 \\
\text{b) } & t = 3600 \tau
\end{align*}
\]

Fig. 1. — The initial configuration and an equilibrated configuration of a 3d percolation cluster of size \( N = 3966 \). At \( t = 0 \), \( R_g = 13 \), while after equilibration it has swollen to \( \langle R_g^2 \rangle^{1/2} = 18 \).
Fig. 2. — The spherically averaged scattering intensity multiplied by \( q^2 \) for 3d percolation clusters of size (O) \( N = 3966 \), (\( \Delta \)) \( N = 1136 \) and (●) \( N = 856 \). The radii of gyration of these clusters after equilibration are 18, 11 and 10, respectively.

Figure 2 shows \( S(q)q^2 \) for 3 clusters of size \( N = 856, 1136 \) and 3966. Here \( S(q) \) is the spherically averaged scattering intensity. We find that on length scales smaller than the radius of gyration, \( R_g \), of each cluster (that is, for \( q > 2\pi/R_g \)), and down to several bond lengths, \( S(q) \) scales roughly as \( q^{-2} \), leading to a fractal dimension of \( d_f = 2.0 \). By plotting the scattering intensity scaled with different powers of \( q \), we find an uncertainty of about 0.1 in \( d_f \). Thus the initial fractal dimension of 2.5 is clearly ruled out. Furthermore, data from the three different clusters overlap in this region, showing that the structure at these length scales is not affected by the finite size of the systems. The oscillations seen in the "flat" region seem to diminish with increased averaging as we found by comparing figure 2 with plots made after shorter simulations. The overshoot in \( q^2 S(q) \) for small \( q \) in figure 2 has also been seen for ring polymers [21] and stars [32].

This swelling effect is similar to the experimental findings of Bouchaud et al. [10] that the fractal dimension of gels near the gelation threshold is reduced [1, 7] form 2.5 ± 0.09 to 1.98 ± 0.03 upon dilution, also in agreement with the Flory theory, equation (1) using \( d_f = 4/3 \) for a 3d percolation cluster. Within our accuracy, we do not see any significant deviations from the Flory theory result.

We also carried out simulations to investigate the structure of several of the 3d clusters for which the repulsive interaction between non-bonded monomers was turned off. We show in figure 3 the resulting \( S(q) \) multiplied by \( q^4 \) for clusters of size \( N = 1136 \) and 3966. One can see the trend to a flat region at \( q > 2\pi/R_g \). However, as the radius of gyration for these clusters is only several bond lengths, the scaling region is very small. We note that the smaller cluster, \( N = 1136 \) has been equilibrated for a total of \( 7 \times 10^6 \Delta t \) and shows very good agreement with the prediction \( S(q) \sim q^{-4} \). The larger cluster was not run as long (only \( 2 \times 10^6 \Delta t \)) and may not be fully equilibrated, which may account for some of the apparent deviations from the \( q^{-4} \) scaling. We found that equilibration in the no excluded volume case
Fig. 3. — The spherically averaged scattering intensity multiplied by $q^4$ for 3d percolation clusters of size (O) $N = 3\, 966$ and ($\Delta$) $N = 1\, 136$ with the excluded volume interaction turned off. The radii of gyration after equilibration are 5 and 3.5, respectively.

was much slower than with excluded volume. Though the scaling region is not large, our data is clearly consistent with a fractal dimension of 4, in agreement with the prediction given by equation (2).

4. Random tethered membranes.

Before we discuss our results for site-diluted tethered membranes, let us first review our results for $p = 1$. We studied systems of size $13 \leq L \leq 55$ using the interaction potential described in section 2. In agreement with the results of reference [17] we find that $\lambda_3 \sim L^2$ and $\lambda_1 \sim L^{1.4}$. For our largest system, $L = 55$, we find that the value of the order parameter $\phi$, defined by equation (4), is 0.85. Thus for this particular potential, which locally is probably a little less flexible than that used by Abraham et al. [17] since it contains no range where the force vanishes, there is relatively little roughening in the transverse direction for the triangular lattice. This roughening increases as the membrane is diluted as seen below.

Figure 4 shows typical configurations for our site-diluted membranes after several million time steps for $p > 1$. Even though the membranes are rough, all but the ones at $p = p_c$ maintain their two dimensional nature. Figure 5 shows the spherically averaged $S(q)$ for the membranes with $p = 0.9$, 0.7 and 0.6. The decay is consistent with $d_t = 2.0 \pm 0.1$. However, in contrast to the results for the three dimensional percolation clusters which exhibited the same fractal dimension due to the swelling of an isotropic object, these membranes are quite anisotropic. As can be seen from table I, $\lambda_1$ appears to decrease slightly as $L$ increases for $p = 0.60$. We believe this is not an indication that the system is not completely equilibrated but is probably a finite size effect. For small $L$, sites removed near the edge play a more important role in locally roughening the system than interior sites (see Fig. 4). In this case $\lambda_1$ could first decrease as $L$ increases before crossing over to its expected behavior for large $L$. Inspection of the ratio $\lambda_3/\lambda_1$ for these membranes
Fig. 4. — Snapshots of the diluted membranes after equilibration. (a) $p = 0.9$, $N = 3422$; (b) $p = 0.7$, $N = 2641$; (c) $p = 0.6$, $N = 2149$; (d) $p = 0.51$, $N = 2093$. All the structures are plotted on the same scale.

Fig. 5. — The spherically averaged scattering intensity for site diluted membranes with (○) $p = 0.9$, $N = 3422$; (△) $p = 0.7$, $N = 2641$ and (●) $p = 0.6$, $N = 2149$. The data for $p = 0.9$ and $p = 0.6$ have been shifted upwards and downwards respectively for the sake of clarity. The arrows show the amount of shift.
(see Tab. I) indicates that they become rougher as $p$ decreases, but $\lambda_1$ remains much smaller than $\lambda_2 \sim \lambda_3$. As one reaches $p = 0.51$, very close to $p_c = 0.5$ the membranes become more isotropic and the values of $\lambda_2$ and $\lambda_3$ are no longer approximately equal. This is seen most clearly from the behavior of the anisotropic scattering functions. Figure 6a shows $S(q)$, $S_1(q)$ and $S_\perp(q)$ for a membrane at $p = 0.51$ with 2093 monomers. In the scaling regime ($q > 2\pi/R_g \approx 0.4$), the three scattering functions converge. In figure 6b the same functions for a $p = 0.7$ membrane are shown. The three scattering functions behave very

Fig. 6. — (a) $S(q)$ (●), $S_1(q)$ (○) and $S_\perp(q)$ (△) for the membrane diluted to $p = 0.51$ with 2093 monomers. (b) Same for the membrane at $p = 0.7$ with 2641 monomers.
differently and converge only at the \( q \)-values that correspond to the length of a single bond. The corresponding scattering intensities for the membranes at \( p = 0.6 \) show a similar behavior. The oscillations in \( S_\perp(q) \) arise from scattering off a 2d planar object with a relatively sharp interface. This has been discussed in detail by Abraham and Nelson [17] for tethered membranes. A similar effect was also seen by Grest et al. [23] in \( S(q) \) for many-arm star polymers.

To quantify the amount of roughness, we measured the order parameter \( \phi \), equation (4). Since for a uncrumpled membrane \( \lambda_3 \) and \( \lambda_3^0 \) both scale as \( L^2 \), \( \phi \) will be nonzero. For a crumpled membrane \( \phi \to 0 \) as \( L \to \infty \). In figure 7 we plot \( \phi \) for our samples as a function of \( p \). Since we were able to study only a few samples for each value of \( p \) due to the slow equilibration of these membranes, we do not know the magnitude of the finite size corrections to \( \phi \), though we do not expect them to be large since our samples are all reasonably large. As expected, \( \phi \) decreases as \( p \) decreases, indicating that the membranes indeed roughen. This is consistent with the plot of the configurations in figure 4. As \( p \) approaches \( p_c \), \( \phi \) has decreased by almost a factor of 3 from its value at \( p = 1 \). Since \( \lambda_3 \sim N^{2/d_t} \) and \( \lambda_3^0 \sim N^{2/1.9} \) for \( p = p_c \) (1.9 being the fractal dimension of the original 2d percolation cluster), we expect \( \phi \to 0 \) as \( L \to \infty \), albeit very slowly. However, since the dependence of \( \phi \) on \( L \) is weak, much larger systems than we can simulate would be needed to check this explicitly. Thus, assuming that for \( p = p_c \), \( \phi = 0 \), we arrive at the conclusion that there must be a first order discontinuity in \( \phi \) as \( p \) approaches \( p_c \). For \( p < p_c \), only finite size clusters (membranes) are present. Thus, site dilution alone, on the triangular lattice is not sufficient to produce a crumpled membrane, though it does have the effect of producing a rougher membrane. Although we have not carried out an explicit finite size scaling, it would be very surprising if for \( 1 > p > p_c \), the membrane would crumple for very large \( L \) and not for \( p = 1 \). This suggests that our results will not change significantly if we had been able to study even larger membranes.

Let us return to the properties of the tethered membranes at \( p_c \). Figure 6a showed that the objects are isotropic as one would expect. The only question which remains is whether it is

![Fig. 7. — The order parameter \( \phi \) (Eq. (4)) as a function of \( p \) for random site-diluted membranes.](image-url)
Fig. 8. — The spherically averaged scattering function multiplied by $q^2$ for 2d percolation clusters at $p = 0.51$ and (O) $N = 832$, (Δ) $N = 1395$ and (●) $N = 2093$. The average radii of gyration for these clusters are 11, 14 and 17, respectively. Also shown is the average $S(q)$ of the three clusters (■) with the same scaling shifted arbitrarily downwards.

Fig. 9. — The spherically averaged scattering intensity multiplied by $q^4$ for membranes diluted to $p = 0.51$ with (O) $N = 832$ and (Δ) $N = 1395$ monomers with the excluded volume interaction turned off.
possible to distinguish the observed result for $d_f$ from the Flory theory prediction $d_f = 2$, equation (1). In figure 8 we present results for 3 membranes at $p = 0.51$. Unfortunately the oscillations in $S(q)$ in each individual sample is large and it is difficult to determine $d_f$ accurately. In the same figure we also present $S(q)$ averaged over the three samples. This is somewhat like what occurs experimentally [10] when the small clusters are removed and the scattering involves an average over the largest clusters. Clearly averaging over only 3 clusters is not equivalent to what occurs experimentally, but it does indicate that one would expect most of the oscillations in $S(q)$ for individual clusters to be eliminated by averaging over a large number of clusters. From either the individual or the average $S(q)$ it is not possible to obtain a very good estimate for $d_f$. The scaling region for these clusters should extend from $q_{\min} = 2 \pi / R_g$ to $q_{\max} = 2 \pi / 3 \approx 2$, where for the upper limit we consider only length scales larger than 3 lattice spacings. Here $R_g \approx 14$ is the average radius of gyration of the clusters and $q_{\min} \approx 0.4$. In this regime $q^2 S(q)$ is approximately flat, suggesting $d_f \approx 2 \pm 0.1$. The upturn for larger $q$ corresponds to length scales smaller than a few lattice spacings and is outside the scaling regime.

For completeness we also studied the 2d percolation clusters imbedded in $d = 3$ with no excluded volume interactions. Results for $q^4 S(q)$ for $N = 832$ and $N = 1395$ clusters are shown in figure 9. Not surprisingly, in agreement to the 3d percolation clusters and equation (2) as discussed in section 3, we find $d_f \approx 4$.

5. Conclusions.

In this paper we have presented results for the spherically averaged and anisotropic scattering function $S(q)$ for gelation/percolation clusters and random tethered membranes. In agreement with Flory theory and neutron scattering experiments, we find that the 3d percolation clusters swell when the excluded volume interactions from their neighboring clusters is removed. This increase is significant and corresponds to a new fractal dimension $d_f = 2$ whereas its original dimension $d_f$ was 2.5 prior to dilution. We also showed that a two-dimensional percolation cluster embedded in three dimensions also has $d_f \approx 2$. We then showed that as one randomly site-dilutes a tethered membrane with a 2-dimensional topology, the objects roughen but remain flat. The amount of this roughness increases linearly as the fraction of sites present, $p$ decreases. However, the membranes fall apart at $p_c$ before they crumple. By comparing the anisotropic scattering functions $S_i(q)$ defined first by Plischke and Boal [16] and $S_\perp(q)$ with the spherically averaged $S(q)$, we showed that 2d tethered membranes at $p_c$ are isotropic while those for $p > p_c$ are anisotropic. A complete treatment of the scattering function $S(q)$ from anisotropic objects has been discussed by Abraham and Nelson [17] and our results are consistent with their analysis.

Gelation/percolation clusters and linear polymers are but two examples of the general class of « polymeric fractals » [1] which have no inherent rigidity. These are objects which are made of polymeric segments at short length scales but have arbitrary self-similar connectivity at larger distances. There are many other objects, for example, diffusion limited aggregates and cluster-cluster aggregates (both reaction and diffusion limited) which satisfy the second criterion, that of self-similar connectivity, but do not swell and change their fractal dimension because they are not made of flexible segments. Most experimental aggregate systems [33], particularly those made from gold or silica, are locally very rigid. It is for this reason that experimentally one does not have to worry about these objects swelling and changing their fractal dimension. However, because $d$ is very near 1 for many of these aggregates (as they contain very few loops), if one could find a way to change the persistence length after they were made, one would expect a reduction in $d_f$ upon swelling for some classes of aggregates. This is particularly true for reaction limited cluster-cluster aggregates in which $d_f \approx 2.1$. 


Though we do not know $d$ precisely for these aggregates, it is probably close to 1.1 and surely less than the percolation value of 4/3. The Flory theory would predict that they should swell and have a new fractal dimension $d_f$ in the vicinity of 1.8. Since this is very near the fractal dimension of diffusion limited cluster-cluster aggregates, these aggregates are not expected to swell very much even if the persistence length of their segments is reduced. While it may be difficult to change the persistence length experimentally after these aggregates are generated, this is quite easy to do using computer generated aggregates. We plan to carry out such a study using the molecular dynamics technique described here.

Acknowledgments.

We thank D. R. Nelson for several helpful discussions and the suggestion that we measure the order parameter $\phi$ given in equation (4). We also thank C. Safinya, T. A. Witten and D. A. Weitz for helpful discussions. MM is a recipient of the Chaim Weizmann postdoctoral fellowship.

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