Swelling of percolation clusters
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Abstract. — The swelling of percolation clusters as models for gelling branched polymers is analyzed by using a simple mean-field approach (for all dimensions) and a Monte-Carlo simulation (for \( d = 3 \), bond fluctuation method). The numerical swelling exponent \( \mu' = 0.443 \pm 0.008 \) shows a significant deviation from the lattice animals solution \( \mu' = 0.5 \), which is caused by the difference between quenched and annealed average procedures.

1. Introduction.

A very important problem for the experimental verification of the percolation as theoretical description of the polymer network formation is the determination of the averaged cluster radius. One possible method uses the analysis of the cluster distribution near the percolation threshold in the sol phase by using the scattering of light, X-rays (SAXS) or neutrons (SANS) [1]. The interpretation of scattering dates in the sol state near the percolation threshold causes annoyance, because the spatial distribution of the clusters overlays the scattering function of the single clusters. Therefore it is reasonable, to stop the network formation near the percolation threshold and dilute the sol by a good solvent. The result of a quasi-infinite dilution are independent clusters and the total scattering-intensity is a simple superposition of the single cluster scattering- functions. The central value of the scattering functions is the mean square radius \( R_N = \sqrt{\langle R^2 \rangle} \) (\( \langle R^2 \rangle \) is the quenched average of the square gyration radius) of the diluted clusters with \( N \) monomers. The quenched average consist of an average over all thermodynamic configurations of a given cluster (with fixed topological structure) and a following average over all possible topological configurations by a fixed number of monomers \( N \).

2. Mean field approximation of the swelling exponent.

For enough large clusters we get the typical scaling relation

\[ R_N = N^{1/b} \] (1)
at the percolation threshold between the cluster radius \( R_N \) and the number of monomers (or bonds) \( N \) \((D\) is the fractal dimension, determined as the inverse product of the critical exponents \(\nu\) and \(\sigma\) \([2] (D = 1/(\nu\sigma))\). This scaling behavior is characteristic for the clusters in the percolation system \([2]\).

On the other hand, one should expected a swelling of the isolated cluster in a good solvent. This situation shows some analogies to the excluded volume problem of linear polymer chains in dense and diluted systems. The excluded volume effect leads to a characteristic swelling of the polymer chain in a good solvent \((R \sim N^{3/(d+2)}\) (Flory-Huggins approximation) for the excluded volume effect, e.g. self avoiding walk, against \(R \sim N^{1/2}\) for vanishing excluded volume effect, e.g. pure random walk). This excluded volume effect is screened in dense systems (polymer melts), e.g. the interaction with other polymer chains leads to a scaling behavior of a Gaussian chain (random walk).

The same excluded volume effect is the cause for the swelling

\[
R_N \sim N^{\mu'} \quad (2)
\]

of the isolated percolation clusters, whereas in the sol state near the percolation threshold a partial screening by other clusters leads to a reduced swelling exponent \(\mu = \frac{1}{D} < \mu'\).

This situation is not identical to the lattice animal problem \([3]\). The latter problem \([4-6]\) disregards the difference between the average over the thermodynamic configurations of one fixed cluster topology and the average over the topology and uses the same statistic for spatial and topological configurations (annealed average). In this case, we get for the swelling exponent 0.641 \((d = 2\), numerical result \([7]\)) and \(\frac{1}{2}\) \((d = 3\), exact result \([8]\)).

Therefore, it is possible to assume, that the expected swelling exponent of swelling percolation clusters is an intermediate case of the two extreme models (radius of the percolation clusters without swelling, lattice animals).

The determination of an upper approximation of the mean-field swelling radius under partial consideration of the quenched topological structure for percolation clusters is possible by using a Flory-Huggins approximation. Therefore, we need the mean square radius \(R_{0,N}\) of a free cluster (without excluded volume effect, for linear chains \(R_{0,N} \sim N^{1/2}\), for statistical branched polymers \(R_{0,N} \sim N^{1/4}\) \([9]\)) with \(N\) monomers. The percolation clusters and the branched polymer chains have similar structure properties, but the topological cycles (which are only present for percolation clusters) should reduce the exponent \(\frac{1}{2}\).

To get \(R_{0,N}\) for a percolation cluster, we separate such a cluster in the backbone (greatest subcluster with two free ends) and dangling ends (subclusters, which are connected only by one bond with the backbone \([10]\) (Fig.1) The backbone contains the mean path (cutting bonds, bons which are single connected, see \([11]\)) and multiple connected bonds (two or more different connections to the mean path), which form typical blobs. For the number of cutting bonds and therefore the number of blobs we get the scaling relation \([11, 12]\)

\[
N_b \sim R_{0,N}^{\frac{1}{2}} \quad (3)
\]

Using \((1)\), equation \((3)\) becomes

\[
N_b \sim N^{\sigma} \quad (4)
\]

The mean path realized a simple random walk with the averaged segment length of the collapsed blob radius for the case of vanishing excluded volume effects, e.g. we get for the free clusters the upper approximation (total collapse of all blobs)

\[
R_0 \sim N_b^{1/2} \sim N^{\sigma/2} \quad (5)
\]
Fig. 1. — Separation of a cluster in the back bone (thick) and dangling ends (thin lines). The backbone decays in the mean path (thick lines) and multiple connected bonds (thick broken lines).

Table I. — Exponents $\mu$ (percolation cluster), $\mu'$ (swollen percolation cluster), $\mu_0$ (free percolation cluster, upper approximation) and $\tilde{\mu}$ (lattice animals) for $R \sim N^{\mu, \mu', \mu_0, \tilde{\mu}}$

<table>
<thead>
<tr>
<th>$d$</th>
<th>$\mu = \sigma \nu$</th>
<th>$\mu_0 = \sigma / 2$</th>
<th>$\mu' = \frac{2+\sigma}{d+2}$</th>
<th>$\tilde{\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.53</td>
<td>0.20</td>
<td>0.60</td>
<td>0.641</td>
</tr>
<tr>
<td>3</td>
<td>0.395</td>
<td>0.22</td>
<td>0.49</td>
<td>0.5</td>
</tr>
</tbody>
</table>

($\sigma / 2 < \frac{1}{4}$, e.g. this upper approximation shows that the partial consideration of the quenched disorder in the percolation clusters may reduce the exponent $\frac{1}{4}$).

An approach of the scaling behavior for the swelling of the percolation clusters is now possible by using the Flory-Huggins method. The free energy of each cluster (mean- field approximation) is determined by the standard formulae \[13\]

\[ F = \frac{R^2}{R_0^2} + \frac{N^2}{R^d}. \]  

(\text{The second term is the usual mean- field contribution of the excluded volume effect, the first term represents the elastic part of the free energy.}) The solution of the problem $F \to \text{min}$ by using (5) is

\[ R \sim N^{\frac{2+\sigma}{d+2}} \]  

contrary to the mean field (Lubensky-Isaacson-) result $R \sim N^{2.5/(d+2)}$ for lattice animals (see the appendix for lattice animals of [2]).

The scaling behavior (7) is only a mean-field approach (which gives only partial contributions from the quenched topological structure) and it is useful, to prove this result by numerical simulations. We analyze the scaling law for three dimensions ($d = 3$) only, a simulation in other dimensions is also possible.

For a first step a sufficient large set of percolation clusters was created at the percolation threshold on a cubic lattice with a simple percolation procedure (number of monomers $N = 2,000$, approximately 50 cluster per $N$).

The second step is the transformation of one cluster to a new stretched cubic lattice (the length of each bond of the cluster is two lattice units, all topological connections are conserved). Each monomer gets a volume of one unit cell (a multiple connection of a lattice site by two or more monomers for this initial configuration is impossible). The gyration radius of this initial condition averaged over all topological configurations gives the radius of the percolation cluster in the sol state $R^\text{perc}_N$

We use the fluctuating bond method [14, 15] for the determination of the isolated cluster radius (thermodynamic average in the equilibrium state). The bonds between consecutive monomers may all have possible length between 2 and $\sqrt{10}$, only $\sqrt{8}$ is not allowed. This set of bonds and the hard core condition (no multiple occupation of a lattice site) guarantees the self avoiding condition and realizes the nonintersection (and therefore the conservation of the cluster topology) in the course of their motion. The monomers move by random diffusion jumps of their monomers to the nearest-neighbor lattice sites under consideration of the excluded volume effect and the bond constraints in a volume with cyclic boundary conditions.

The average of the resulting gyration square radius in the equilibrium over all topological

Fig.2. — Quenched averaged square radius $R^\text{perc}_N$ and $R^\text{isol}_N$ as function of monomers $N$. The slopes of the lines (result of a linear regression) are 0.795 for $<R^2>_N|^\text{perc}$, 0.886 for $<R^2>_N|^\text{isol}$ and 0.091 for the ratio $\sigma_{\text{diff}} = <R^2>_N|^\text{isol} / <R^2>_N|^\text{perc}$.
different configurations for a given \( N \) determines \( R_N^{\text{isol}} \). Figure 2 shows the dependence of the quenched averaged gyration radius \( R_N^{\text{perc}} \) (initial configurations, percolation clusters in the sol) and \( R_N^{\text{isol}} \) (equilibrium value). We get for \( R_N^{\text{perc}} \) an exponent \( \mu = 0.398 \pm 0.008 \) (\( R_N \sim n^\mu \)) and for the equilibrium value of the isolated cluster \( \mu' = 0.443 \pm 0.008 \). Note, that the error is determined from the standard deviation of the linear regression procedure.


The numerical simulations corroborate the results of the mean-field approximation for the scaling behavior swelling of percolation clusters. The exponent \( \mu' = 0.443 \) is a result of the quenched average and has a value between the exponent of the percolation clusters in the sol \((0.395)\) and the lattice animals exponent \((0.5)\). Note, that the difference between the predicted swelling exponent \( \mu' = 0.49 \) and the numerical value \( \mu' = 0.443 \) is a result of the mean-field approach.

On the other hand, the topological cycles produce an effective collapse against the statistical branched polymer (mean-field swelling exponent \( 0.5 \)). The change of the swelling exponent from the result of the annealed average (lattice animal) to the quenched average has an essential importance for the experimental proof of the percolation theory as model for the network formation. Only the result of the quenched average allows a correct interpretation of scattering dates, from which the universality class and that of the determination of other scaling exponents (by using scaling relations) follows. The identification of swollen clusters with lattice animals, found often in the gelation literature, thus seems dangerous.

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References