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Topological Entanglements in the Percolation Problem

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Topological entanglements play an important role in the physical properties, such as viscosity, of macromolecular structures. We investigate the likelihood of the appearance of entanglements in the bond percolation problem. We show that *below* the percolation threshold p_c (but extremely close to it) there exists an entanglement threshold p_e. Between p_e and p_c, there exists an infinite spanning group of interlocked (linked) clusters. The achieved numerical resolution of $p_c - p_e = (1.8 \pm 0.4) \times 10^{-7}$ required averaging over an extremely large number of configurations.

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An important problem of the statistical mechanics of macromolecules is how to account for topological entanglements.[1] A solution of ring polymers behaves differently from a solution of linear polymers, since a pair of such rings created separately is prevented from interpenetrating by topological constraints, while a pair of rings which have been created in an interlocked (linked) state (catenanes[2]) cannot be separated without breaking up the macromolecules. Theoretical approach to the problem requires an addition of constraints to the standard statistical mechanics of polymers.[3] The presence of these constraints splits phase space into mutually inaccessible regions, and generates a purely entropic elastic response.[3-5] Topological entanglements play a crucial role in rubber elasticity.[6] Note that in the gel formation process[7] the viscosity may become infinite (while the shear modulus will become finite) *even in the absence of a single molecule (infinite cluster) spanning the entire system,* since it suffices to have a spanning group of interlocked (linked) clusters to produce that effect. Self-entangled ring molecules and pairs of entangled molecules have been extensively investigated.[8] Prior to this work no information was available on the importance of entanglements in more complicated systems, such as branched polymers, and the treatment of the physical properties of such structures (e.g., elasticity[9] near the gel point) completely disregarded the effects of entanglements.

In this work we take a first step towards the understanding of the role played by entanglements in a standard three-dimensional percolation problem.[10] Our attention is focused on the geometrical/topological aspects of the problem. We show that below the usual percolation threshold p_c, there exists a distinct *entanglement threshold* p_e, which is the relevant critical point for the problems of viscosity and entropic elasticity. While the distance $\Delta p_{ce} \equiv p_c - p_e$ is not a universal property, the main result of this work is establishment of the fact that it *does not vanish.* In the considered system (independent bond percolation on a simple cubic lattice) the distance between the critical points Δp_{ce} is extremely small, and we had to resort to extremely large statistics (averages over millions of configurations) on small and moderate-size lattices to resolve that quantity. While we

argue that Δp_{ce} will be small in most standard percolation models, in the presence of short-range correlations this separation may become significantly larger.

In a regular percolation problem bonds belong to the same *connectivity* cluster (c-cluster) if there is a continuous path of present bonds connecting them. If the probability p for bonds to be present exceeds the threshold value p_c, an infinite c-cluster is present in the system. We will say that two bonds belong to the same entanglement cluster (e-cluster) if they either belong to the same c-cluster, *or* belong to different c-clusters which cannot be separated without violating the topological constraints. One should keep in mind that entanglement is a global property, which cannot be detected by a simple inspection of the local environment of each bond. Moreover, one might have a situation, resembling Borromean rings,[4] where a triplet of c-clusters is entangled, while each pair of that triplet, viewed separately, is not entangled. Our primary goal is finding the entanglement threshold p_e, above which there exists an infinite e-cluster. From the definitions it is clear that the $p_e \leq p_c$; the purpose of our work was the establishment of the strict inequality $p_e < p_c$.

One should bear in mind a formulation of the same question in terms of plaquette percolation[11]: Consider a dual of the bond percolation problem, in which we place a plaquette in the middle of each absent bond, perpendicular to it. The concentration of the plaquettes will be $q = 1 - p$. One can easily understand the meaning of the threshold value $q_c = 1 - p_c$ by considering a large finite system: If the bonds do not percolate in, say, the vertical direction, one can find a collection of plaquettes forming an *orientable* surface separating the system into upper and lower parts. Thus the threshold q_c signifies the appearance of infinite orientable surfaces in the system. This surface will not, in general, be *simply connected.* Moreover, if $p_e < p_c$, then in the range $q_c < q < q_e = 1 - p_e$ all infinite surfaces will have handles. The threshold q_e will therefore signify the appearance of the first infinite simply connected surface.

We use a finite-size scaling, or large-cell Monte Carlo renormalization-group,[12] approach to determine the difference between the critical points: For a finite $L \times L \times L$ lattice we define a contact probability $X_c(p,L)$ that a system percolates in, say, the z direction. This quantity can be viewed as a probability for a bond to be present, in a system which has been rescaled by a factor of L. The fixed point $p^*(L)$ of such renormalization-group transformation is determined from the equation $X_c(p^*,L) = p^*$, and provides an estimate of p_c. [The trivial (stable) fixed points, $p^* = 0$ and $p^* = 1$, are excluded from the discussion.] For $L \to \infty$ we expect that $p^*(L) \to p_c$. Similarly, we can define a probability $X_e(p,L)$ that the system is entangled (i.e., either percolates *or* cannot be separated into two parts without violating the constraints) in the z direction, and use this function to obtain an estimate $p_e^*(L)$ of the entanglement threshold p_e. One can easily see that the expected distance between the estimates of the critical points $\Delta p_{ce}^* \equiv p^* - p_e^*$ is extremely small: The smallest possible entangled configuration on a cubic lattice consists of two interpenetrating (but not touching) loops of sizes 2×2 each. This minimal configuration consists of sixteen bonds, and its probability for $p \approx \frac{1}{4}$ will be smaller than $p^{16} \simeq 10^{-10}$. Thus for $L \leq 2$ entangled configurations are impossible, while for $L \simeq 10$ we expect to have very small Δp_{ce}^*. (The numerical simulations indeed show that $\Delta p_{ce}^* \simeq 10^{-8}$-$10^{-7}$ in the relevant range of L's.) However, we may take advantage of the fact that X_c and X_e almost coincide: In the vicinity of p^* both curves can be treated as straight lines, as depicted in Fig. 1. To first order in $p - p^*$ these lines are parallel, with slope $\alpha(L) \equiv [\partial X_c / \partial p]_{p=p^*}$. Thus, instead of measuring the horizontal distance Δp_{ce}^* between the lines, we can measure the vertical distance $\Delta X \equiv X_e(p^*,L) - X_c(p^*,L)$. From Fig. 1, one can see that $\Delta p_{ce}^* = \Delta X/(\alpha - 1)$. Since $\alpha \simeq 10$ in the relevant range, the quantity ΔX is larger than Δp_{ce}^* by an order of magnitude, and, therefore, more easily measurable. ΔX is just the probability of finding a nonpercolating, yet entangled, realization for given L and p.

We considered lattices with $L = 4$, 6, 12, and 18. On those lattices we examined 192.3, 40.3, 6.3, and 2.7 *millions* of configurations, respectively. The total simulation consumed 119 d of CPU time on an Apollo Model DN 3000 minicomputer.[13] Since the program demanded relatively small memory, but required enormous execution times, the large redundancy of the data structure has been used to accelerate the calculation. Simulations

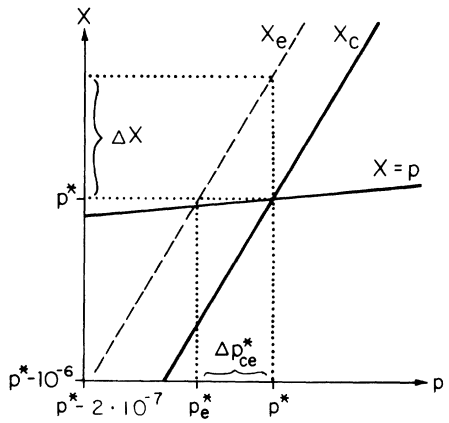

FIG. 1. Qualitative plot of the entanglement probability X_e (dashed line) and the percolation probability X_c (solid line) as functions of p, in the vicinity of p^*. Fixed points are determined from the intersection of those lines with the solid line $X = p$. Only part of the graphs in the vicinity of p^* is shown. Typical scale for $L \simeq 10$ is shown. Notice that in this case ΔX is larger than Δp_{ce}^* by an order of magnitude.

were performed at $p^*(L)$.[14] All nonpercolating realizations have been examined for entanglements: Initially all loops were identified and recorded with an algorithm resembling the burning method,[15] which systematically searches structures, and identifies branching points and the points at which these loops are closed. Pairs of loops belonging to different clusters were then examined for entanglements. One should keep in mind that ΔX is extremely small in the considered range of L's, and therefore, it sufficed to examine only "direct" entanglements between the loops belonging to the cluster attached to the upper boundary of the lattice and the loops belonging to the cluster attached to the lower boundary—the probability of entanglement via an intermediate cluster is completely negligible. The presence of a topological link between two loops l_1 and l_2 was established by the calculation of the Gaussian invariant,[16]

$$\mathcal{L}_{12}=\frac{1}{4\pi}\oint_{l_1}\oint_{l_2}\frac{(d\mathbf{r}_1\times d\mathbf{r}_2)\cdot(\mathbf{r}_1-\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|^3}. \quad (1)$$

If the (integer) result of this double integration does not vanish, the loops are linked. $\mathcal{L}_{12}$ does not discriminate well between different kinds of links. In particular, there exist entangled (linked) configurations for which $\mathcal{L}_{12}$ vanishes.[17] Thus, in principle, this method of calculation would only establish a lower bound on ΔX. However, even the simplest entangled configurations with vanishing $\mathcal{L}_{12}$ contain so many bonds that in the considered range of L's their probabilities are negligible (and many orders of magnitude below the accuracy of our calculation). Thus, within the accuracy of our results, we obtain the actual value of ΔX, rather than its lower bound.

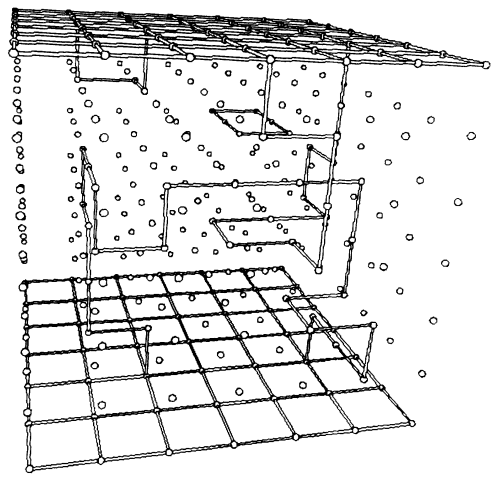

FIG. 2. Typical entangled nonpercolating configuration for $L=6$. The spheres represent the lattice sites, and the cylinders represent the relevant bonds. The z axis has been chosen as the direction of percolation/entanglement. The boundary conditions used in the simulation are evident in the filling of the top and bottom planes with bonds. All small loops and dangling bonds (without large loops) have been removed for clarity.

Evaluation of $\mathcal{L}_{12}$ does not involve a calculation of continuous line integrals, since it can be reduced to intersection counting on the projections of the loops on an arbitrary plane.[18] Nevertheless, the number of operations required to evaluate the expression is proportional to the product of the lengths of the loops. Figure 2 depicts an entangled nonpercolating configuration on $L=6$ lattice found by our program. For clarity, all small loops and irrelevant dangling bonds have been removed. Such "shaving" of the configuration is actually performed by the program itself in order to minimize the number of Gaussian invariants which must be calculated. Among the millions of examined configurations for each L only $\simeq 10$ entangled nonpercolating configurations were found. Thus, the accuracy of our estimates of ΔX and Δp_{ce}^* is only about 30%. Figure 3 depicts the sequence of estimates $\Delta p_{ce}^*(L)$ as a function of $1/L$. The estimated asymptotic value is $\Delta p_{ce}=(1.8\pm 0.4)\times 10^{-7}$. While the distance between the critical points is very small, there is not much doubt that it is finite.

The accuracy of the measurement can be increased by use of larger cells. We expect that for very large lattices the time consumed for complete analysis of a single configuration will increase as L^8. However, in our measurements it increased approximately as L^3 because of numerous simplifications resulting from the use of small L. The rapid increase in time is partially compensated by an increase in ΔX (because of an increase of the slope α). Thus the time needed to find an entangled configuration increased very slowly. For $L=18$ we needed 87 h CPU to find a single entangled configuration. From our data we estimate that for $L\approx 300$ most of nonpercolating configurations at p^* will be entangled. However, one should keep in mind that for such large cells one will need more elaborate methods of link detection, and en-

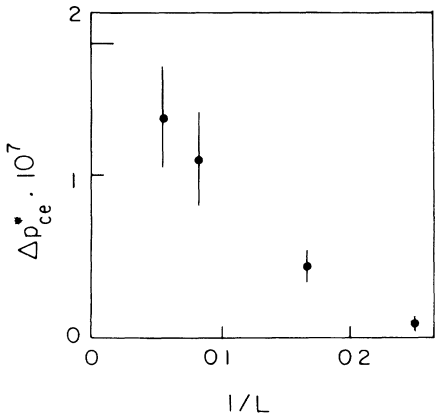

FIG. 3. Successive distances between the fixed points Δp_{ce}^* as a function of inverse cell size $1/L$. Error bars are the estimated standard deviations due to the finite number of realizations. The extrapolation of the graph to $1/L=0$ (as indicated by the horizontal bar) gives the distance between the percolation and entanglement thresholds.

tanglements between a pair of e-clusters "mediated" by an additional cluster will also play an important role.

Geometrical characteristics of the detected e-clusters differ from those of c-clusters.[19] However, such an extreme closeness of two critical points prevents investigation of the critical properties of e-clusters near $p = p_e$ for such small cells. The nonlocal nature of the entanglement constraint, and the possibility of entanglements consisting of more than a single pair of loops, lead to the expectation that the critical properties at p_e will be different from those of the c-clusters at p_c. The discrete nature of *lattice* percolation requires the presence of rather large loops (i.e., being close enough to p_c) before entanglements become physically possible. In lattices with large coordination numbers (e.g., the simple-cubic lattice with nearest-neighbor and next-nearest-neighbor connections) one may have rather small entangled loops; however, the increase in the coordination number decreases the p_c and it does not seem to be possible to separate the critical points further. One might consider further investigation of the critical properties near p_e using percolating systems with short-range correlations.

It is interesting to observe that the presented problem is specifically *three dimensional*—it has no two-dimensional analog. In more dimensions *linear* loops cannot be linked. One can, however, imagine entanglements among objects of higher topological dimension (e.g., pairs of surfaces, or surfaces with lines). It is unclear whether such objects appear in more-dimensional percolation problems, and what the proper generalization of this problem is to an arbitrary dimensionality.

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