Growth and arrest of topological cycles in small physical networks

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Editted by Angel Rubio, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany, and approved June 8, 2020 (received for review April 3, 2020)

The chordless cycle sizes of spatially embedded networks are demonstrated to follow an exponential growth law similar to random graphs if the number of nodes $N_x$ is below a critical value $N_x^*$. For covalent polymer networks, increasing the network size, as measured by the number of cross-link nodes, beyond $N_x^*$ results in a crossover to a new regime in which the characteristic size of the chordless cycles $h_\ast$ no longer increases. From this result, the onset and intensity of finite-size effects can be predicted from measurement of $h_\ast$ in large networks. Although such information is largely inaccessible with experiments, the agreement of simulation results from molecular dynamics, Metropolis Monte Carlo, and kinetic Monte Carlo suggests the crossover is a fundamental physical feature which is insensitive to the details of the network generation. These results show random graphs as a promising model to capture structural differences in confined physical networks.

Results and Discussion

A number of simulation methods have been used to model the covalent structure of polymer networks, both with and without explicit spatial embedding. These include kinetic Monte Carlo (12–14) (KMC), graph-driven statistical models (15, 16), Metropolis Monte Carlo (17, 18) (MMC), and molecular dynamics (MD). In this work, end-linking polymer networks were generated with a quenched MMC approach, which creates a spatially embedded network by assigning edges that have a small length in Cartesian distance and simultaneously satisfy the chemical constraints of the polymer chains and cross-linker molecules. That is, a regular network is created where edges (polymer chains) are assigned to nodes (cross-linker molecules) such that each node has the same degree (covalent bonds per molecule) of $f_x$. An example snippet of a polymer network is shown in Fig. 1A. The influence of finite-size effects was then studied with a series of simulations where the number of nodes $N_x$ is varied from 50 to 5,000. The values of $f_x$ and $N_x$ were independently varied, while the number of edges was fixed as $N_x f_x/2$ to maintain a stoichiometric mixture of polymer chains and cross-linker molecules. The size of the simulation cell was scaled to maintain a constant monomer density of $\rho = 0.85$ for all simulations. Five independent replicas of each $f_x-N_x$ pair were created, and the chordless cycles were determined for each network. Reference calculations with kMC and MD were carried out to verify the MMC predictions. For further comparison, random networks were generated with similar values of $f_x-N_x$, in which the only constraints were a regular distribution of the node degree. For all networks, we take the maximum of the distribution of chordless cycle sizes as a characteristic mesh size $h_\ast$ (19) and study the relationship of $h_\ast$ with $N_x$. (See Materials and Methods for details.)

The mesh size of random and polymer networks is shown in Fig. 1B for $f_x$ in the range of three to eight (20). For small values of $N_x$, both types of networks are seen to follow an exponential law of the form $N_x(h_\ast) = \alpha \beta^{h_\ast}$, where the parameters $\alpha$ and $\beta$ depend strongly on the node degree $f_x$. Increasing $f_x$ leads to a rapid decrease of $h_\ast$, which is consistent with analytical predictions for other measures of shortest cycles in random networks (21). As $N_x$ increases, the physical constraints of the polymer networks enforce a crossover to the bulk behavior in which $h_\ast$ reaches a plateau value at $y_\ast$ and the corresponding number of nodes $N_x$. Increasing $N_x$ beyond $N_x$ does not change the mesh size. The mesh size distributions corresponding to the arrest of $h_\ast$ are shown in Fig. 1B, Insets, where each curve is found for spatial network | thermoset | polymer topology

Author contributions: T.W.S. designed research, performed research, analyzed data, and wrote the paper.

The author declares no competing interest.

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Data deposition: Supporting data and procedures can be accessed at Figshare (DOI: 10.6084/m9.figshare.12276626).

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www.pnas.org/cgi/doi/10.1073/pnas.2006305117

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April 3, 2020

Edited by Angel Rubio, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany, and approved June 8, 2020 (received for review April 3, 2020)
one value of \( N_* \); the relations of \( f_x \) with \( y_* \) and \( N_* \) are shown in Fig. 1C.

Importantly, correlations can be established between the bulk mesh size \( y_* \) with the number of nodes at the crossover \( N_* \), as well as the parameters of the exponential law (\( \alpha \) and \( \beta \)). This connection is widely useful, as it allows the presence of finite-size effects to be predicted from the number of nodes in the physical network, a quantity that can be estimated from experiments. Further, the intensity of the finite-size effect (for those networks with \( N_* < N_* \)) can be understood by treating the small physical network with the exponential law given above for random networks. As demonstrated in Fig. 2, both \( N_* \) and parameters \( \alpha \) and \( \beta \) are related to \( y_* \) through a power law dependence. For the regular spatial nets considered here, the minimal number of nodes to capture the bulk structure is in the range of about 400 to 16,000, depending on the bulk mesh size, and follows a power law of the form \( N_* \approx y_*^{1.7} \).

In the case of polymer networks, the effect of a related measure of chordless cycle size, the smallest loop size, has been shown analytically and numerically as a negative correction (e.g., see ref. 22) to the elastic modulus. In other materials, the nature of the physical constraints can be expected to change the details of the finite-size behavior, particularly if the mesh size or other topological features cannot be reduced in size due to chemical considerations such as unfavorable bond angles, steric hindrance, or chain stiffness. Nonetheless, the result given here suggests that descriptions of random networks, like those given in Fig. 2, can incorporate confinement effects into equations of state or constitutive laws that explicitly include the topological structure of the forces. Thus, continued work in this area has potential for a broad analogy of small physical and random networks that informs material properties under confinement.

Materials and Methods

Simulation Details. Polymer networks use the usual freely jointed bead-spring model for polymer chains with Lennard-Jones dynamics described by Kremer and Grest (23). The beads of each linear chain interact through the truncated shifted Lennard-Jones potential \( U(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] + (\sigma/r)^{12} + (\sigma/r)^{6} \), where \( \varepsilon \) and \( \sigma \) are chosen as unity, and the force cutoff

\[ r_i = 2^{1/6} \] All bonds were represented with the finite extensible nonlinear elastic (FENE) potential, \( U_{FENE}(r) = (-K r_0^2/2) \ln(1 - (r/r_0)^2) \), with \( r_0 = 1.5\sigma \) and \( K = 30\varepsilon/\sigma^2 \). Each system was created with a self-avoiding random walk of monodisperse chains of length \( N = 32 \) mixed with a stoichiometric number of single cross-linker beads at a density of \( \rho = 0.85 \). The systems were then equilibrated with dynamics under periodic boundary conditions for \( 10^3 \tau + 1,000N^2\tau \) with a time step of 0.005\( \tau \). The chain ends form, at most, one new bond (\( f_x = 2 \)), while each cross-linker bead can form a bond with as many as \( f_x \) linear chains, where \( f_x \) is varied from three to eight. These systems correspond to cross-link density, taken as \( 2\rho/(Nf_x) \), in the range of 0.0066\( \sigma^{-3} \), to 0.0177\( \sigma^{-4} \), where \( \sigma \) is the monomer size. The system size was varied by creating a series of 21 networks with values of cross-linker number \( N_* \) spanning the range 50 to 5,000 and a corresponding number of beads ranging from 2,450 to 645,000. The ratio of the edge length of the simulation cell to the chain radius of gyration was between 5 and 40 for all networks. (24).
Simulation Methods.

Random networks. The method of Steger and Wormald (25) was used to generate networks with a uniform degree \( d \) equal to the cross-linker functionality. 1 The network of \( N \) nodes is created with no edges. 2 A list of unique pairs of nodes is created and maintained such that the degree of any node is at most \( d - 1 \). 3) A pair of nodes \( u, v \) is selected from the list with probability proportional to \( (d - d(u))(d - d(v)) \). 4) The edge is added to the network. 5) Steps 1 to 4 are repeated until all nodes have the same degree \( d \).

Simulated annealing optimization. A tempered MMC optimization was used to generate network structures (18). Stoichiometric mixtures of \( N_c \) cross-linkers and \( N_l \) linear chains were relaxed at constant volume with a density of 0.85. The network connectivity was then assigned using the simulated annealing method, which minimizes the total length of the newly created bonds. Bond swap and bond translation moves were considered. Both moves were accepted with probability taken from a harmonic energy penalty, \( P(x) = \exp(-x^2) \). No other restrictions were considered. Five independent structures with different network connectivity were prepared for each pair of \( f_c - N_c \).

Other reference calculations. A rejection-free kMC algorithm was adapted from recent work of Wang et al. (14). The algorithm checks the probability of closing a chain across networks molecules under the assumption of Gaussian behavior, including self-connections.

Dynamics. Networks were grown with reactive, dynamic simulations based on local bonding rules. The bonding rule was chosen strictly such that cross-link bonds are created only if reactive monomers directly contact one another, that is, the collision cross-section is chosen as a fixed value of 

\[ R = 2^{1/6} \sigma \]  

(26, 27). A stoichiometric mixture of \( N_w \) chains and \( N_c \) cross-linker beads was distributed in the simulation box; the mixture was equilibrated well above the glass transition temperature at \( T = 1.0 \beta / k_B \) cross-link bonds were formed during dynamics when the reactive sites approached within \( 2^{1/6} \sigma \) until the system reached 97.7% cure. All dynamic simulations used the Large-scale Atomic/Molecular Massively Parallel Simulator package (28).

Cycle counting. Chordless cycles were taken as a closed walk on nonrepeating nodes in which no interior edges serve as a shorter chord connecting two nodes of the cycle. The identified chordless cycles are identical to the irreplaceable shortest path rings identified by Matsumoto et al. (29). In practice, this was carried out by recording, for each node, the shortest paths between all pairs of the node neighbors that are closed without a chord, up to a cutoff distance varied between 10 and 25 edges. Redundant instances of the same cycle were eliminated with homology tests, resulting in a single record of each chordless cycle and its size \( h \). Self-loops and second-order cycles were directly counted as \( h = 1 \) and 2, respectively. Multiple edges were considered as follows: A node \( i \) with one or more repeating edges \( N_e \) to a neighboring node creates at least one second-order cycle, where the number of induced cycles is related to the number of redundant edges as \( N_e / 2 \).

For cycles of order three or more, any second-order cycles internal to the main cycle were treated as a single edge. Supporting data and procedures can be accessed at http://doi.org/10.6084/m9.figshare.12276626.

ACKNOWLEDGMENTS. I thank Robert M. Elder, Berend C. Rinderspacher, and Randy Y. Mrozek for useful discussions. The US government is authorized to reproduce and distribute reprints for government purposes notwithstanding any copyright notation hereon.

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