Networks in Soft Matter: Analysis and Order Parameters

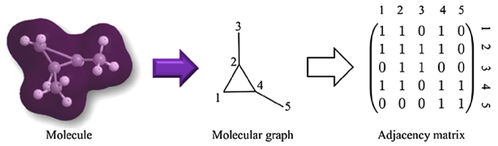
Abhishek K. Sharma and Juan J. de Pablo

Pritzker School of Molecular Engineering, The University of Chicago, Chicago, Illinois, USA

THE UNIVERSITY OF CHICAGO
PRITZKER SCHOOL OF MOLECULAR ENGINEERING

Graph Theory + Molecules

In recent decades, computational chemists have used graph theory to analyze networks present in a variety of contexts where the edges might represent a physical or a conceptual connection.



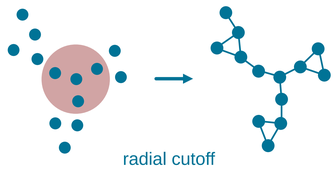
molecular graphs

chemical reaction networks

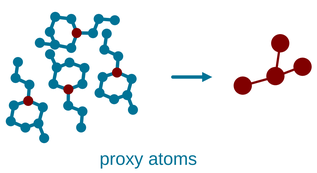
networked polymers

More recently, network science has matured as a field with impactful applications in communications, social sciences, and logistics. In this poster we illustrate a few use cases of advanced network science tools in soft materials.

Mapping Molecular Simulations to a Graph



radial cutoff

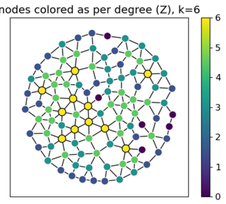


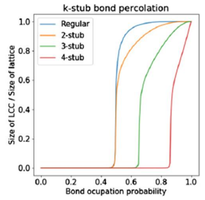
proxy atoms

If we are interested in intermolecular interactions, a simulated configuration of molecules could be translated into a graph by considering a cutoff distance for each atom/bead, with any neighbors forming edges of the graph. The cutoff could be varied to study different properties of interest. However, this procedure could become cumbersome for larger systems comprising complex molecules, and it may necessitate choosing representative atoms for each molecule as a proxy. For even larger systems where atoms and molecules are too numerous, it might be more prudent to histogram the configuration onto a lattice-grid to obtain a density distribution, which can conveniently be unwrapped as a graph of a square or cubic lattice, where each cell becomes a node.

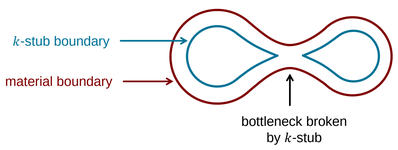
k-stub Decomposition

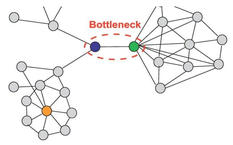
A k-stub is a part of the network where nodes have a minimum number of k connections. It highlights the portion of the network that is well-connected, which could be of significance for certain applications. We have found that it is particularly useful to consider the family of networks obtained by changing k. As k is increased, it gets rid of poorly connected regions in the network, which generally comprises of the surface, bottlenecks, and dendrites.





If the largest connected component size is measured for each value of k, called LCC_k, we can trace the robustness of percolation: connectivity at high k implies the percolation is more robust. This reflects in the bond percolation thresholds for square lattice increasing with increasing k.



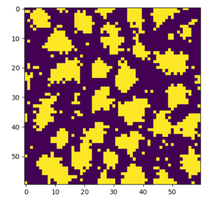


For a physical system, a k-stub meaningfully peels back the layers of the system. The value of k at which the system abruptly stops percolating provides measure of bottlenecking.

Applications

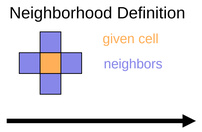
An Order Parameter for Continuity

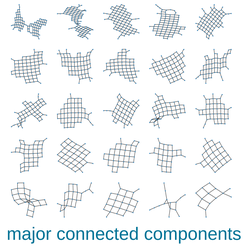
The $k - LCC_k$ curve can be used as a composite order parameter that can interpolate between states of robust continuity and discreteness. For instance, bicontinuous phases such as gyroid phase in diblock copolymers can be characterized by the connectivity. If they are forming from a spatially discrete phase (such as BCC), we can track the formation of bridges with a "leading edge" at the lower values of k. Here I illustrate this approach for a square lattice gas. First, we convert the lattice into a graph based on a defined neighbor definition.



Active Cells

Inactive Cells

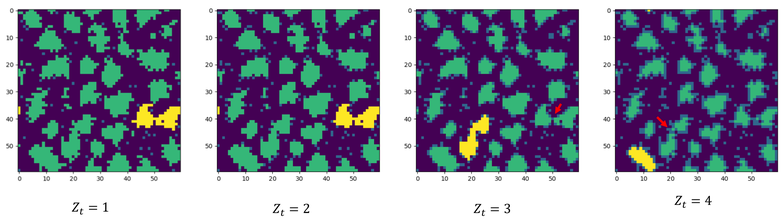


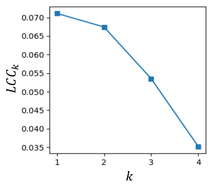


major connected components

We can then apply k-stub decomposition on this graph and measure the size of the largest connected component k-stub relative to the size of the graph.

largest connected component (LCC), k-stub not in LCC, active cells not in k-stub, inactive

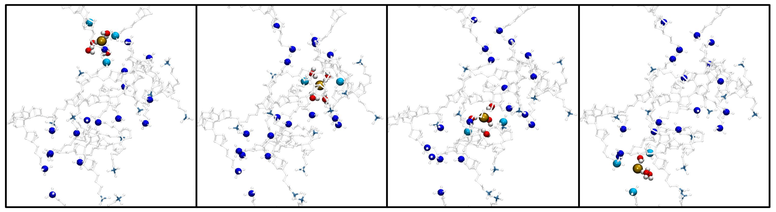




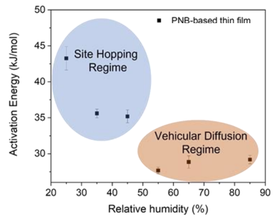
Increasing k breaks narrow bridges between domains, thus domains that might be the largest get split (see red arrows ↑) into smaller sections if they are not compact. Consequently, LCC_k is monotonically decreasing. This curve can then be used to characterize the level of connectivity in the system. For instance, one may use the curve as an order parameter to bias the system to a certain level of connectivity at various levels.

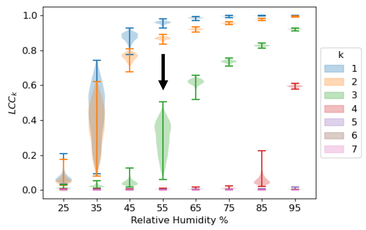
Ion Transport in Anion Exchange Membranes

We can apply k-stub decomposition to study materials where connectivity has consequences on physical properties of the material. For example, anion exchange membranes undergo a sharp increase in ionic conductivity at specific relative humidities, presumably due to percolation of ion channels comprising water molecules. We converted this system through picking representative atoms from channel forming moieties (water and ions), and then applying a radial cutoff based on the first peak of $g(r)$ to define edges. KSD reveals that this transition takes place when channels are robust at $k = 3$ level, enabling vehicular transport of ions.



ion transport through a channel of water and polar residues of the polymer

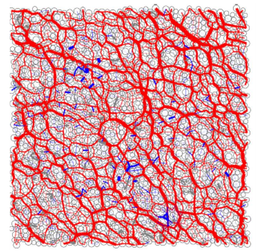




Network Analysis of Dense Granular Suspensions

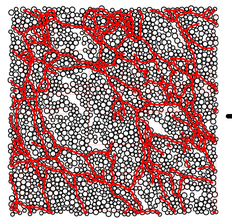
Force Chain Networks

Networks also arise in the context of dense granular suspensions with frictional constraints. Under stress, the frictional contacts generally emerge as force chains - quasi-linear structures that effectively support the incident stress. The properties of this force chain network could clarify the rheological properties such as shear thickening and jamming of such suspensions.

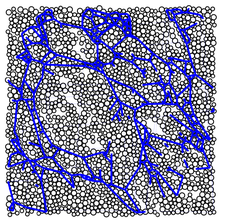


Coarsening

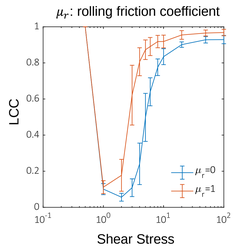
The structure of the force chain network is such that is useful to understand the network at a coarser level. The load redistribution primarily happens at hubs where multiple struts meet. This coarsening reduces the size of the graph and makes the computation faster.



force chain network



coarsened network



This coarsening allows for identification and characterization of individual force chains. Properties of interest include linearity, composition, and length. Introduction of different kinds of frictional constraints, such as sliding, rolling or twisting friction could lead to a change in the properties of the network, reflecting in a change of rheological properties of the suspension. For instance, introduction of rolling friction (μ_r) leads to an early onset of shear thickening, which correlates with an increase in LCC of the force chain network.

Conclusions and Next Steps

We have shown contexts where network science tools could be used in the context of percolation/connectivity problems, and in force chain networks in dense granular suspensions. In future, we intend on using techniques such as community detection, stochastic block models, and centrality measures to understand other contexts where networks arise. For instance, recent developments in optimized disordered networked metamaterials prompts how functionality is learnt by the network.

The algorithms developed here for k-stub decomposition for percolation and connectivity in molecular systems will be made openly available as a part of the PySAGES package. The algorithms are currently being adapted for GPU-based computing.

Modified versions of the k-stub algorithm could be utilized for detection of nuclei of bicontinuous phases arising in particulate and bicontinuous systems, or to promote discretization in metastable continuous states.

Acknowledgements

These research projects were executed in collaboration with Abhinendra Singh (CWRU), Fernando Escobedo (Cornell), Ge Sun (UChicago), Joshua Mysona (Argonne), and Ludwig Schneider (UChicago)

References

- Blay, V., García-Domenech, R., & Gálvez, J. (2017). Problem solving with Molecular Topology: a walkthrough. *ChemTexts*, 3(2), 1-5.
- Elder, R. M., & Sirk, T. W. (2017). Topological structure and mechanics of glassy polymer networks. *Soft matter*, 13(45), 8392-8401.
- Arman Mohseni-Kabir et al. "Percolation thresholds for robust network connectivity". *Journal of Statistical Mechanics: Theory and Experiment* 2021.1 (2021), p. 013212.
- Singh, A., Ness, C., Seto, R., de Pablo, J. J., & Jaeger, H. M. (2020). Shear thickening and jamming of dense suspensions: the "roll" of friction. *Physical Review Letters*, *124*(24), 248005.
- Weichao Shi et al. "Aperiodic bricks and mortar mesophase: A new equilibrium state of soft matter and application as a stiff thermoplastic elastomer". *Macromolecules* 48.15 (2015), pp. 5378–5384.

email: abhisheksharma@uchicago.edu
website: abhishekksharma.com