An interdisciplinary approach in understanding the polymerization process with random graph models

Introduction

In this article we present the results of an interdisciplinary project in mathematics and chemistry. The goal of our team, which consisted of five mathematicians and three theoretical chemists, was to develop a mathematical model in order to study a chemical process called polymerization. This type of research contributes to the improvement of interdisciplinary studies, which yield new research opportunities. This research does not only provide us with in-depth knowledge, but also with new communication channels between math and chemistry, something valuable for further research. We will now present our research and the results that we gained.

As mentioned above we are interested in a chemical process called polymerization, this is a chemical process where monomers are small molecules that connect with each other to become polymers. During this process, which is called *polymerization*, the matter existing of these monomers undergoes a *phase transition* from liquid to solid. While the groups of monomers are small, the matter is liquid, when enough connections are made between the monomers, the matter turns solid and consists of mostly polymers.

To be able to better understand and predict the properties of polymers, we are interested in their structure. An example of where this understanding could be helpful is in the drying process of paint, which is a polymerization process. After a long period paint starts to degenerate whereby polymers break down. To understand the behaviour of polymers we investigate the polymerization process, and in particular the structure of the polymers near the phase transition point; the point where the transition from liquid to solid starts happening.

For chemists it has thus far not been possible to understand this process exactly. Several approaches have been made, using experiments and by using differential equations, but no success has been booked.

Therefore we will approach this problem from a different angle. We compare the polymerization process with random graph models, which turn out to behave very similar in the phase transition. First we compare it to a configuration model and secondly to the Erdős-Rényi random graph model.

Polymerization

Our method to study polymerization relies on a mathematical construction called random graphs. These graphs consist of nodes and edges between these nodes, which in our case will represent respectively monomers and chemical crosslinks between these monomers. To incorporate chemical restrictions in the random graph model, we use a degree distribution acquired from the chemical process.

The degree distribution gives us for every node the number of links this node is going to form. We incorporate this degree distribution in our model by assigning half-edges to the nodes. The number of half-edges we assign to a node is equal to the degree of this node. Now, we can start placing edges between the nodes, by selecting a set of two half-edges uniformly at random and connecting them [1]. This process is independent off the distance between the selected half-edges. As more nodes are connected, larger connected components emerge and, finally, a *giant component* emerges. This is the largest component of the system and is of the order of the system size. In this construction the concept of a giant component is used to represent large polymers that emerge during applications, like the drying process of paint.

Since polymerization is a process evolving over time, in which the state of the system is constantly changing, the degree distribution is also not constant over time. The probability distribution describes only the chemical system at time t and not the system at time $t+1.$ Therefore, we acquire multiple degree distributions by taking several snapshots of the chemical system through time. These consecutive snapshots of the polymerization process can be studied independently of each other in order to understand how the process evolves, and more specifically when the giant component emerges.

Configuration model and phase transition

We study the consecutive snapshots using a specific random graph construction, called the configuration model. In this way we can use results from this static configuration model regarding the existence of a giant component in order to understand the emergence of a giant polymer. What we are looking for is a necessary condition such that a giant component exists in a configuration model with a given degree sequence. What would such a condition look like? First of all we expect it to depend only on the degree sequence. Let's first investigate when a giant component does not emerge. If for example all the degrees are equal to one, then the graph consists solely of components of size two. This means that a significant amount of nodes should have degree larger than one in order for a giant component to emerge. If you have nodes with degree either one or two then we also don't expect components to grow large. Hence we need a significant fraction of points with degrees strictly larger than two. In [2] the authors formalize this argument and prove there exists a condition on the degree sequence that is sufficient and necessary. Let λ_i denote the fraction of nodes of degree i. Then, given a degree sequence $D,$ define the quantity $Q(D)$ as follows

$$Q(D) = \sum_{i>0} i(i-2)\lambda_i.$$

It turns out that if $Q(D)$ is greater than zero, there almost surely emerges a giant component in the graph obtained by the configuration model with input $D.$ If $Q(D)$ is smaller than zero, the opposite holds.

By repeatedly checking this condition for the degree distributions we obtained from the chemical system at different times, we can find out when such a giant component arises. And when such a giant component exists it contains almost all nodes. Using this result we can determine when a phase transition occurs in the configuration model which we subsequently use in order to determine when the phase transition occurs In the polymerization process.

This Is one aspect of the process we want to understand, namely when the phase transition occurs. This gives an answer to the question when the phase transition happens but we also want to understand how the transition actually happens. How is the giant component formed?

Erdős – Rényi random graph and the critical window

To understand how the giant component is formed we will consider a small interval around the point where the phase transition occurs. For simplicity of the arguments we present the result for a simpler random graph model than the configuration model, namely the ER model. It turns out though that both models behave in a similar way regarding the structure of the components around the phase transition. In the ER model, instead of considering a fixed degree for every node we let every node be connected to any other node with probability $p \in [0,1]$. More specifically we consider the case $p = \lambda/n$ where λ is a positive number. In this model every node has on average a degree that is equal to λ.

We study three different regimes [2]: the subcritical regime $(\lambda < 1)$, the critical window $(\lambda = 1)$ and the supercritical regime $(\lambda > 1)$. In the subcritical regime all the components in the random graph are relatively small and about the same size, namely $O(ln(n))$. However, once we look in the supercritical regime, the random graph contains a giant component of size linear in n. Note that only a small shift in p,from $(1-\varepsilon)/n$ to $(1+\varepsilon)/n$ with $\varepsilon > 0$, has a crucial influence on the structure of the random graph. Choosing $\varepsilon \to 0$ with a given speed allows us to also analyze the case $\lambda = 1$, which is called the critical window. This case is much more complicated to analyze and many results have been derived yielding a deeper understanding of the phase transition in this simpler model. With L_i we denote the i'th largest component in the random graph. The following result are obtained from the ER-model.

The regimes	
The Subcritical Regime	
Parametrization	- $p = \frac{1-\varepsilon}{n}$, with $\varepsilon = \lambda n^{-\frac{1}{3}}$, $\varepsilon = o(1)$ and $\lambda \to \infty$. - Example: $p = 1/n - n^{-4/3}n^{0.01}$.
Component sizes	- $L_1 = \Theta(\varepsilon^{-2}\ln\lambda) = \Theta(n^{2/3}\lambda^{-2}\ln\lambda)$. - $L_k \sim L_1$ for all fixed k.
The Critical Window	
Parametrization	- $p = \frac{1\pm\varepsilon}{n}$, $\varepsilon = \lambda n^{-\frac{1}{3}}$, λ a real constant. - Example: $p = 1/n \pm 2n^{-4/3}$
Component sizes	- $L_k = \Theta(n^{2/3})$, for the largest k (k fixed) components.
The Supercritical Regime	
Parametrization	- $p = \frac{1+\varepsilon}{n}$, $\varepsilon = \lambda n^{-\frac{1}{3}}$, $\varepsilon = o(1)$ and $\lambda \to \infty$. - Example: $p = 1/n + n^{-4/3}n^{0.01}$.
Component sizes	- $L_1 \sim 2\varepsilon n = 2\lambda n^{2/3}$. - $L_2 \sim \Theta(\varepsilon^{-2}\ln\lambda) = \Theta(n^{2/3}\lambda^{-2}\ln\lambda)$.

The last question to answer is how to go back to the configuration model given these results for the ER-model. These results have been derived for the CM as well and it has been shown that the structure and the size of the components for both models in the phase transition behave similar. It is

still an open problem if we can directly build a bridge between these two models and a lot of research is being carried out in this direction.

Conclusion

To understand the phase transition in polymerization we use random graph models. The configuration model describes the polymer structure at a certain time step, based on the degree distribution that we obtained from the chemical system at that moment. For a certain degree distribution we found a condition that tells us whether or not the giant component arises.

Subsequently we looked at the ER-model to find out more about the component sizes in the different regimes. For $\lambda < 1$ all the components are of size $O(ln(n))$ and for $\lambda > 1$ a giant component arises.

This new approach in understanding polymerization has given us a lot of new insights, however it also has left us with a lot of questions. For example, we are not sure how the knowledge gained from the ER-model can be implemented in the configuration model. Moreover it can still be questioned if the configuration model is representative for polymerization. Finally we left out certain conditions, such as the distance between monomers, which could be of influence on the process. Further research in this field is therefore be of great importance.

Section 6 Bibliography

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