

## MONTE CARLO TYPE INVESTIGATIONS ON THE NUCLEATION PROCESSES IN SOFT MATTER SYSTEMS

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Using Monte Carlo simulations, we investigated the sporadic nucleation of polymers and the results were compared with those obtained from the Avrami equation. From the simulation data, we calculated the overall crystallization rate constants and the Avrami indices. We considered isotropic growth of the nuclei in 1,2 and 3 dimension, the obtained results for the Avrami indices being in excellent agreement with theory and experiments. We also investigated the dependence of the overall crystallization rate constant on the crystallization velocity.

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### 1. Introduction

Contrasting to micro-molecular substances, as a subfield of soft matter systems, polymers consist of long, linear or branched chains, covering a broad distribution of molecular lengths. It follows that not all of molecular architectures are suitable to give regularly shaped crystals in the solid state. Usually, polymers solidify as very tiny crystals dispersed in an amorphous matrix and interconnected by disordered chains randomly disposed [1,2]. In polymer solutions or melts, the macromolecules are entangled, giving rise to bunches of interpenetrated random chains. It follows that the task of packing these long coiled molecules into crystal may be very difficult and the process is not total, the correct term used for polymers being semicrystalline materials [1-4].

The crystallization process of small molecules is a well known two steps mechanism [5]. The first step, or the nucleation phase, consists in the formation of a nucleus of the crystalline phase. If the sizes of the formed nuclei are greater than a certain critical size, this step is followed by the growth step, consisting in growing of such nuclei. In the case of small molecules, the process is not generally hindered and it develops until the degree of crystallinity eventually becomes equal with one.

As it is conceptually explained in [2], the property of semicrystallinity of polymers may be understood as follows. Due to the fact that polymer molecules are very long, at a certain temperature, they may have a huge number of equilibrium conformations, translated in a complicated landscape of entropy and free energy. In the first stage of the crystallization process, a nucleus is formed by monomers coming from different locations of the folded polymeric chain, or even from different chains. In the next step, the step of growing, there will be a competition between these heterogeneous nuclei to incorporate monomers not yet fixed in the crystalline state. On the other hand, the number of equilibrium conformations of the incorporated macromolecules dramatically decreases, the entropy of the chain also decreases, giving a big set of barriers in the free energy landscape (a typical characteristic of the soft matter systems). It follows that there may be a number of monomers belonging to different macromolecules that cannot enter in the

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crystalline state, remaining in the amorphous state. Thus, the polymer in the solid state is always only semicrystalline, because the crystals are never completely filling the volume.

The kinetics of crystallization of polymers is based on the appearance and growth of crystalline regions which expand over the volume of the polymer during the transformation.

Physico-chemical and technical properties of solid polymers are influenced by their structure, which, in turn, is determined by the development of the process of crystallization [1-4]. Therefore, the crystallization of polymers has been both experimental and theoretical studied for many years, but the understanding of the process is difficult due to the particularities in terms of structure for different polymers.

Understanding the kinetics of crystallization of polymers is very important for the manufacturing process and controlling of the finished product properties. Mechanical, electrical, optical properties and thermal stability - all of them depend on the crystal size distribution and the degree of crystallinity.

Experimental techniques for studying the crystalline polymers are carefully addressed [6] and they include: X-ray diffraction, polarized light microscopy, electron microscopy, NMR or Raman scattering. For analyzing the degree of crystallinity, density and calorimetric methods (also in combination with X-ray scattering) are especially used.

During the years, much effort has been devoted in optimizing the theoretical description of the crystallization process in soft matter.

The macroscopic study of the crystallization process is based on recording the evolution of the crystalline fraction of the material,  $X_c$ , as function of the time [1-4, 6]. The standard method of analyzing the phase transformation of polymers is based on the now classical Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [7-11]. Starting from the probabilistic method of Kolmogorov, continuing with the mean field approximation of Johnson and Mehl, Avrami assumed that the semicrystalline polymer structure may be described by a two-phase model: a crystalline and a liquid phase.

The Avrami method relies on the mechanism of nucleation and growth and consists on the following assumptions [12]:

- the space volume of the crystallization is infinite and homogenous;
- the homogeneity of the space implies that nuclei may appear anywhere in the space, *i.e.* not only in the non-transformed region, but also in the already transformed one; these non-physical nuclei were called phantom nuclei, or simply phantoms;
- all the nuclei spherically grows with the same velocity;
- two growing nuclei may mutually invade each other, like in Fig. 1;

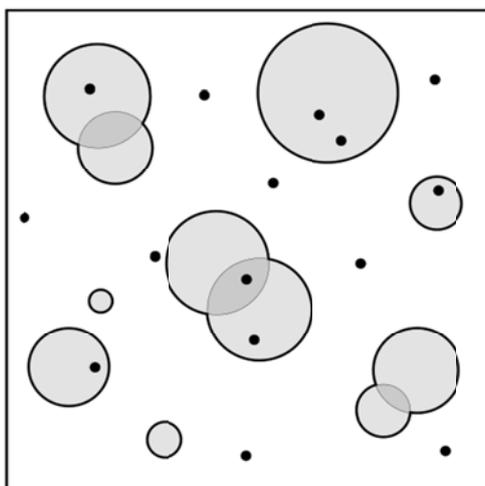


Fig. 1. Mechanism of nucleation and growth in the JMA approach.

It is explained in [12] that phantom nuclei do not affect the true value of the non-transformed volume fraction of the material, because a phantom exist in the nucleus containing it

and do not contribute to the increase of the transformed volume fraction. If two growing nuclei have superposed regions, the superposed volume should be counted only once in the transformed volume fraction.

Without awareness about intimate molecular mechanism involved in the crystallization process, the Avrami equation gives convenient means of empirically describing crystallization and the results of the model are in very good agreement with the experimental facts [1-4, 6].

Although exact calculations based on the Avrami equation have been made, the same results may be obtained by computer simulations. In recent years, computer molecular modeling became a useful tool in the investigation of polymers [13, 14], as well as in analysis and solution of problems associated with crystallization [15, 16].

In the present paper, we used Monte Carlo simulation in order to better understand and analyze and the process of polymer crystallization.

## 2. Molecular Model and Simulation Method

The Avrami method, which hypotheses were described in the introductory part of this paper, is applicable to any type of crystallization process, not only for polymers as a soft matter system. There are two approaches for addressing the crystallization of polymers [17]:

1. athermal nucleation, sometimes called instantaneous nucleation: all the nuclei are formed at the beginning of the crystallization and start to spherically grow at constant rate;
2. thermal nucleation, sometimes called sporadic nucleation: the nuclei are formed at a constant time rate and are uniform disposed in the volume of the probe. The already formed nuclei again grow at constant rate.

Because here we are interested only in thermal nucleation, we will briefly present here its main results.

Since it is assumed that crystallization starts randomly at different locations and propagates outwards from the nucleation sites, the process may be described as follows [6, 17]: if raindrops randomly fall on the surface of water and create expanding circular waves, what is the probability that the number of waves passing a representative point P up to time t is exactly n?. The problem was solved by Poisson and is referred to as the Poisson distribution:

$$P(n) = \frac{\exp(-E)E^n}{n!} \quad (1)$$

where E is the average number of the average value of the number of waves passing a point P.

The number of waves  $dE$  which pass through the point P for nuclei within the spherical shell  $r, r + dr$  is [17]:

$$dE = 4\pi r^2 \left( t - \frac{r}{v} \right) I dr \quad (2)$$

where v is the growth velocity of the nuclei and I is the number of nuclei which appear in the unit time per unit of volume. The assumption is that we work in the 3- Dimensional space.

The probability that no wave fronts pass at the point P is:

$$P(0) = \exp(-E) \quad (3)$$

If we denote by  $X_c$  the crystalline fraction of the material,  $P(0)$  is equivalent with the volume fraction of the polymer which is still in the molten state [4]:

$$P(0) = 1 - X_c \quad (4)$$

If we integrate firstly equation (2) and insert the result in equation (3) and (4), we obtain [17]:

$$1 - X_c = \exp\left(-\frac{\pi l v^3}{3} t^4\right) \quad (5)$$

The coefficient of time and its exponent depend on nucleation and growth mechanism, then equation (5) may be rewritten in the Avrami form:

$$1 - X_c = \exp(-kt^n) \quad (6)$$

with  $k = \frac{\pi l v^3}{3}$  - the overall crystallization rate constant and  $n$  - the Avrami index.

The Avrami index may be considered as being composed by two terms [18]:

$$n = n_d + n_n \quad (7)$$

where  $n_d$  represents the dimensionality of the growing crystals and  $n_n$  represents the time dependence of the nucleation (in our case it is 1). For instantaneous nucleation, the Avrami equation has a similar form, but this coefficient is then 0 [6,17].

In our Monte Carlo simulations, we consider the sporadic nucleation of a polymer in a cubic box of length  $L$ . During the run, we randomly throw nuclei inside the volume of the box, at a constant rate,  $I$ , and all the nuclei were spherically grown with the same velocity,  $v$ . Through the simulation, we recorded the volume percent of the crystalline fraction of polymer,  $X_c$ , at every time step. The last quantity was calculated as the ratio between the volume occupied by spherulites (taking account of possible overlapping) and the volume of the box.

In order to avoid fluctuations, the process was repeated for a 100 cycles and we used averaged data for processing.

### 3. Results and discussion

The first set of simulations were performed in a cubic box with length  $L = 40$ , at a nucleation rate  $I = 1$  and at a growing velocity  $v = 0.5$ . The dependence of the volume fraction of the polymer as function of time is depicted in Figure 2. Its sigmoid behaviour is identical with the theoretical one predicted in [17] on the basis of the Avrami equation (6).

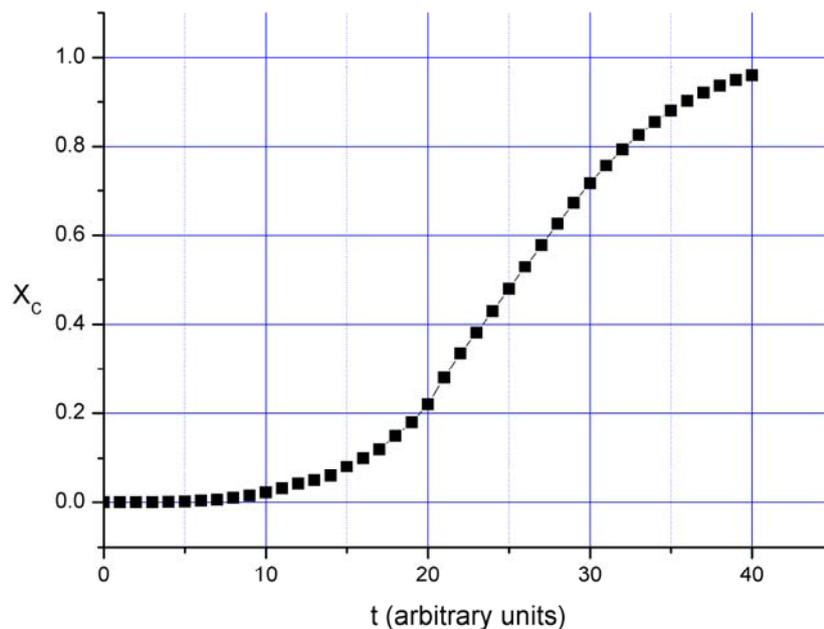


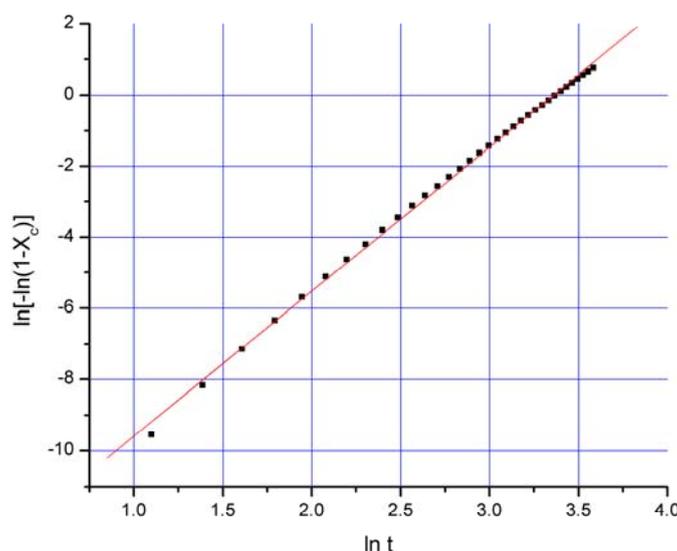
Fig. 2: Volume fraction of the polymer as function of time for a cubic box with  $L = 40$  and  $v = 0.5$ . Lines are only guide to the eyes.

We have to notice that the crystalline fraction of polymer obtained in our simulations, as well as those predicted by Avrami equation (6), asymptotically tend towards 1 (in our simulation towards 100%, since we expressed the volume fractions as percentage). As we explained in the introductory part, the real polymers are only semicrystalline, because the crystals are never completely filling the volume. This discrepancy may be explained by the simplifications of the Avrami model and by the observation from [6], according to which the real nucleation of a polymer is a mixture of athermal and thermal nucleation.

The main goal of the Avrami equation is to obtain the overall crystallization rate constant,  $k$ , and the Avrami index,  $n$ . These may be directly calculated by using methods similar to those described in [19, 20], but the results are more precise and easier to obtain if equation (6) is linearized by taking the double logarithm [1-4, 6, 17]:

$$\ln[-\ln(1 - X_c)] = \ln k + n \ln t \quad (8)$$

If the left side of the equation (8) is represented as function of  $\ln t$ , we obtain a line with the slope equal with the Avrami index, while the intercept equals the logarithm of the crystallization rate constant. The graph in figure 3 is the linearization of the simulated data from figure 2 conditions.



*Fig. 3: Representation of the equation (8) for a cubic box with  $L = 40$  and  $v = 0.5$ . The red line represents the linear fit of the data.*

The linear fit gives  $n = 4.06 \pm 0.02$  and  $\ln k = -13.64 \pm 0.02$ . Taking into account that the simulation was for a 3D cubic box, the value of  $n = 3 + 1$  is in excellent agreement with the value predicted from theory [6, 17, 18].

The nucleation rate and the growing velocity of the nuclei are the main parameters which drive computer simulations of the crystallization process. We investigate the role of the growing velocity by repeating the simulations for same simulation box and nucleation rate and for a range of growth velocities from 0.1 to 1. The results are depicted in Fig. 4 and a summary of the data is presented in Table 1.

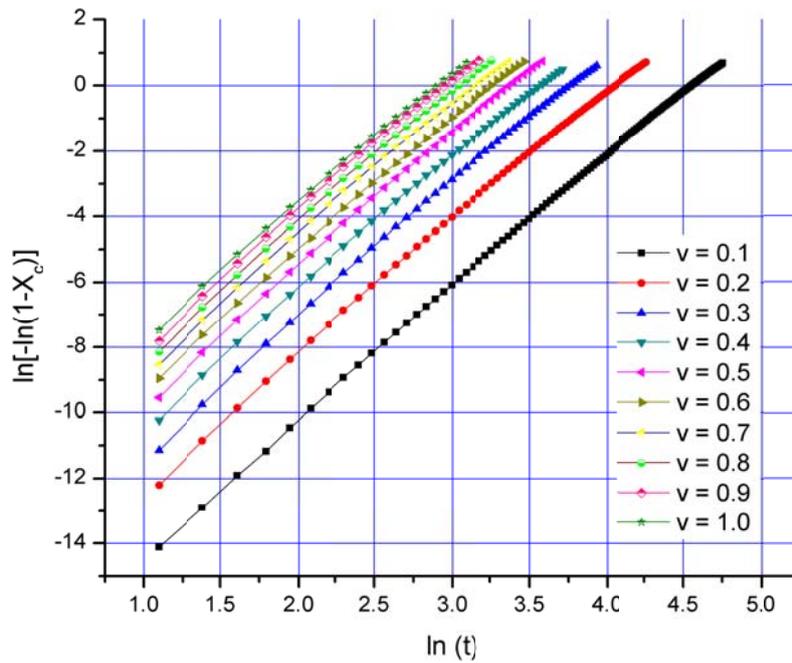


Fig. 4: Representation of the equation (8) for a cubic box with  $L = 40$  at several growth velocities. The lines are linear fits for each set of data.

Table 1. Avrami index and nucleation rate as function of nuclei growth velocity

Simulation No.	v	n	ln k	k*10 <sup>6</sup>
1	0.10	3.99	-18.12	0.01
2	0.20	3.99	-16.09	0.10
3	0.30	4.04	-15.11	0.27
4	0.40	4.01	-14.22	0.66
5	0.50	4.06	-13.64	1.19
6	0.60	4.04	-13.13	1.98
7	0.70	4.00	-12.57	3.47
8	0.80	4.05	-12.29	4.59
9	0.90	4.07	-11.97	6.33
10	1.00	4.04	-11.68	8.46

From Figure 4, we see that all the fitted lines are parallel to each other, with a slope approximately equal with 4, as it is expected for Avrami equation in a 3D space. They differ at the intercept, which, according with equations (6) and (8), depends on the growing velocity.

If we draw the plot of crystallization rate as function of  $v^3$ , we find a linear dependence as in Figure 5 and as it is expected for the coefficient k from the Avrami equation.

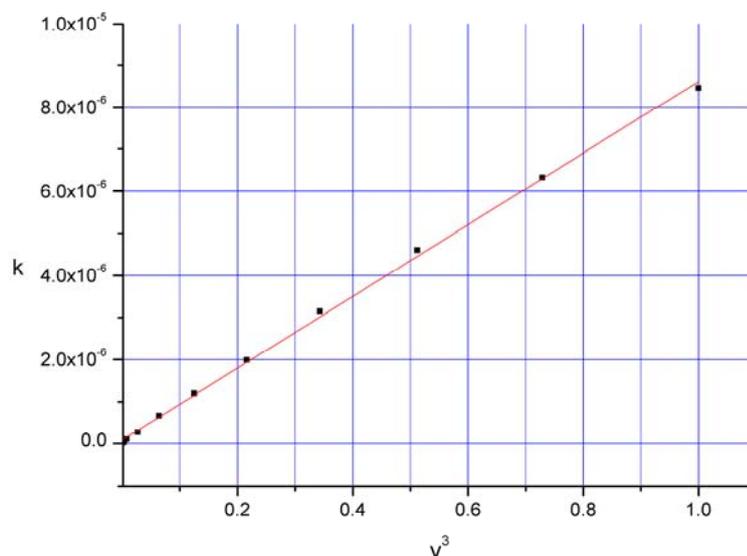


Fig. 5: Dependence of crystallization rate as function of  $v^3$ .  
The line is linear fit of data.

Using two modified versions of our computer program, we also made simulations for 2-dimensional and 1-dimensional systems. For the two dimensional system, we found the Avrami index  $n = 2.982 \pm 0.002$  and for the one dimensional system, the value was  $n = 1.99 \pm 0.07$ . Both results entirely match with equation (7), which states that, for sporadic nucleation,  $n$  represents the space dimensionality plus 1 (from time variable). The results for the low dimensional spaces (and especially for the 1-dimensional system) are in perfect agreement with the theory [6, 17], giving a true insight about the universality of the Avrami model as a valuable theoretical tool used in investigating soft matter systems.

#### 4. Conclusions

Monte Carlo simulation is a important instrument for analyzing the kinetics of crystallization of polymers. Our computational models provided excellent results and confirm the predictions of the Avrami equation that theoretically describes the crystallization process.

From the simulation data, we calculated the overall crystallization rate constant and the Avrami index. The most important parameter, the Avrami index, was obtained in accordance with the theoretically prediction  $n = n_d + n_n$  for usual 3-Dimensional space, but also for 2-Dimensional and 1-Dimensional spaces. The key conclusion is that the Avrami equation is universal valid and can be applied for processes in 3D space as well as for in plane thin films (2D) or thin rods/filaments (1D) soft matter systems.

For the usual cubic box, we also systematically investigated the dependence of the overall crystallization rate constant on the crystallization velocity. We found that the dependence is on the 3-th power of  $v$ , as is calculated from theory.

A drawback of the computer program is that it predicts, for a sufficient long run, a crystallization degree equal to the unity. Although the results are in accordance with those of the Avrami equation, both the approaches suffer - as the polymer in the solid state is always only semicrystalline (because the crystals are never completely filling the volume). The explanation consists in simplifying the assumptions of the Avrami model presented in the second section of the paper and also used in our computer simulations. To overcome this problem it was proposed a modified version of the Avrami equation [6, 17]:

$$1 - \frac{X_c}{X_{c\infty}} = \exp(-kt^n) \quad (9)$$

where  $X_{c\infty}$  is the finally reached volume crystallinity.

In order to better complement with the real systems, the simulation programs may be easily adapted for further using equation (9) with  $X_{c\infty}$  obtained from experimental data like DSC (Differential Scanning Callorimetry) and dilatometric methods.

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