

INVESTIGATION OF POLYMER NUCLEATION PROCESS IN N-DIMENSIONAL SPACE

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We extend the Kolmogorov–Johnson–Mehl–Avrami theory for the instantaneous nucleation of polymers to a multi-dimensional space, obtaining a generalized Avrami equation. We demonstrate that the Avrami index is equal with the space dimension, the same as for the classical case. The equation of the overall crystallization rate constants is obtained as function of the growing velocity and nuclei concentration. The results were achieved by means of computer simulations, by studying the instantaneous nucleation mechanism of a polymer situated in a multi-dimensional space. The simulations were in very good agreement with the deductions obtained from theory.

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1. Introduction

In a series of papers, we investigated the nucleation of polymers using Monte Carlo simulation [1-3], and the results were compared with those obtained from Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [4-8]. As already explained [1, 2, 9-12], the crystallization kinetics of polymers is based on the generation and growth of crystalline regions that expand over the volume of the polymer during the transformation.

As described in [13] and [14], the first step of the nucleation consists in the formation of a nucleus of the crystalline phase, by creating of a series of centers in the polymer volume. There are two ways of formation [14]:

1. instantaneous nucleation, when, at the beginning of the crystallization process, all nuclei randomly appear in the volume of the polymer. This step is followed by the symmetrically grow with constant rate of all the nuclei.
2. sporadic nucleation, when the nuclei appear in the volume of the polymer with a constant time rate and are also uniform placed in space. These nuclei grow as well symmetrically, with a constant rate.

The investigation of the dynamics for the crystallization process consists in recording the time evolution of the material crystalline fraction, X_c [1-3, 9-14] and applying the KJMA theory [4-8]. The theory shows that the time dependence of X_c has the form of the Avrami equation:

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

where k is the overall crystallization rate constant and n is the Avrami index [14].

These constants depend on the type of nucleation and on the dimensionality of the space where the crystallization takes place [1, 2, 13, 14]. The Avrami index is equal with the dimension of the crystallization space for the instantaneous nucleation and with dimensionality of the space plus one for the sporadic case.

In our previous papers devoted to investigations of the polymers crystallization by computer simulations [1, 2], we found the results summarized in the table below:

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Table 1. Avrami index as function of the nucleation type and dimensionality of the space. The values are from [1, 2] and are approximate, as they resulted from simulations.

Space dimension	Instantaneous nucleation	Sporadic nucleation
1-dimensional (linear growth)	1	2
2-dimensional (circular growth)	2	3
3-dimensional (spherical growth)	3	4

In all the above presented situations, the growth of the nuclei was symmetrical and completely free. The results are fully compatible with those from [13, 14]. On the other hand, we also investigated the crystallization of systems that are geometrically hindered, that we labeled as frustrated systems [3]. We found that for a sufficient long time from the beginning of the nucleation, the frustration is manifested by the decrease of n by one or two unities, depending on the frustration type (upon one or two dimensions).

This behaviour of the Avrami index led us to the supposition that this type of dependence is an universal law and, possibly, it would be valid for multidimensional spaces. Such an environment for the polymeric growth can only be represented (at this point) by a mathematical model. By means of computer simulations, we investigate in this manuscript the instantaneous nucleation of a polymer in the case of an n -dimensional space.

2. Molecular Model

In order to develop the simulation method, we have to rewrite the classical Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [4-8] in the framework of an n -dimensional space. We keep all the assumptions of the classical Avrami method already used in our previous papers [1, 2] and explained in [13, 14], adapting them to the multidimensional geometry:

- the n -dimensional space volume of the crystallization is infinite and homogenous;
- the space where the crystallization takes place is homogeneous, meaning that the nuclei randomly appear in the volume of the crystallization;
- all the nuclei symmetrically grow with the same velocity; in the classical theory for the 3-dimensional space follows that the growth is spherical, in the 2-dimensional space is circular, whereas for the n -dimensional space is an n -dimensional hypersphere.
- two growing nuclei may mutually invade each other; this behaviour was explained in [1, 15] and was kept for the studied situation.

In order to obtain the time dependence of the crystalline fraction, we follow a procedure similar to that in [13, 14]. The theory assumes that instantaneous crystal growth is identical with the following situation: at a certain moment of time, said initial moment, a number of raindrops randomly fall on a surface of water and each of them creates one leading expanding circular wave. We want to obtain the expression of the probability that the number of waves that pass a certain point, P , up to time t is c . According to [14], the solution is given by the Poisson distribution:

$$P(c) = \frac{\exp(-E)E^c}{c!} \quad (2)$$

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

Since all the nuclei are created at the same moment, $t = 0$, and grow with same velocity, v , the average number of crystal fronts passing through point P at the moment t is [2, 13, 14]:

$$E(t) = V_n(r)g \quad (3)$$

where $V_n(r)$ is the volume of the n -dimensional sphere of radius $r = vt$ and g is concentration of the nuclei, *i.e.* the number of nuclei per unit volume.

Taking into account the expression of the volume of an n-dimensional sphere [16], the average number is:

$$E(t) = \frac{\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2}+1)} (vt)^n g \quad (4)$$

with $\Gamma(x)$ being the gamma function.

If X_c is the crystalline fraction of the polymer, the volume fraction of the polymer which is still in the molten state may be seen as the probability that the point P has not been touched yet by a wave-front:

$$P(0) = 1 - X_c \quad (5)$$

Using equations (2), (4) and (5), we obtain:

$$1 - X_c = \exp\left(-\frac{\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2}+1)} v^n g t^n\right) \quad (6)$$

As in [1-3, 13, 14], the coefficient of t^n is denoted as the overall crystallization rate constant:

$$k = \frac{\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2}+1)} v^n g \quad (7)$$

and equation (6) may be rewritten as the classical Avrami equation (1).

We remark that, as stated in [13] and [14], the crystallization rate constant linearly depends on the number of nuclei per unit volume, g . It also depends on v^n instead of v^3 (for the 3-dimensional space).

Using the recurrence expression for the gamma function $\Gamma(x+1) = x\Gamma(x)$, with $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$ and $\Gamma(1) = 1$, we may calculate any value of $\Gamma\left(\frac{n}{2}+1\right)$, [17]. For example, in the 3-dimensional space, we obtain $k = \frac{4}{3}v^3g$, the same value as in [2] and [14], directly obtained from the 3-dimensional space.

3. Results and discussion

In order to verify the above considerations, we used Monte Carlo simulations to investigate the instantaneous nucleation of a polymer in a hyper-cubic box of length L situated in an n-dimensional space. The employed simulation programs are comparable with those in [1-3]. Since the nucleation is instantaneous, at the beginning of the run, the nuclei were randomly generated in the simulation box. Then, all the spherulites were grown with the same velocity v . At every subsequent time step, we calculated the ratio between the volume occupied by spherulites (taking account of overlapping) and the total volume of the box, obtaining the crystalline fraction of polymer, X_c .

In figure 1, we present the result for the simulation of a crystal growth in a hyper-cubic box with length $L = 5$ in a 7-dimensional space, at a growing nuclei velocity $v = 0.05$ and with the number of nuclei $s = 150$. In this case, the concentration of nuclei is $g = 1.92 \cdot 10^{-3}$ nuclei/unit of volume.

The shape of the curve X_c as function of time is of sigmoidal type, similar with the results for the usual 3-dimensional space, as predicted by theory and experimentally verified [13, 14], and also obtained by Monte Carlo simulation [1-3].

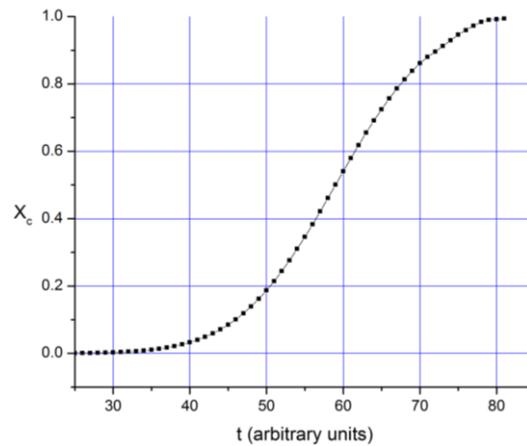


Fig. 1: Volume fraction of the crystallized polymer as function of time for a cubic box with $= 5$, growth velocity $v = 0.05$ and concentration of the nuclei $g = 1.92 \cdot 10^{-3}$ nuclei/unit of volume. The dimensionality of the space is 7.

As for the classical situation, the curve depicted in Figure 1 may be linearized by taking double logarithm of equation (1):

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

From equation (8), we notice that quantity $\ln[-\ln(1 - X_c)]$ depends linearly on $\ln t$, the slope of the line being the Avrami index, while the intercept is the logarithm of the crystallization rate constant.

The graph in Figure 2 is the linearized representation of the data from Figure 1.

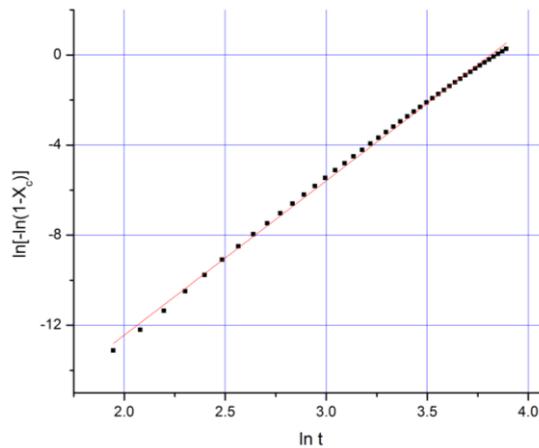


Fig. 2: Representation of the data from Figure 1 using equation (8). The red line represents the linear fit of the data.

The linear fit of our simulated data gives $n = 6.956 \pm 0.061$ and $\ln k = -26.496 \pm 0.200$, these results being in very good agreement with the values predicted from equations (6) and (7) for the 7-Dimensional space.

In order to prove the universality of the Avrami equation, we made simulations for a wider range of space dimensionalities. All the simulations were performed in a hyper-cubic box with length $L = 5$, the number of nuclei was $s = 150$ and the grow velocity is indicated in the Table 2. The values of the Avrami index and logarithm of the crystallization rate constant are shown in

Table 2. We obtained for all simulations that the Avrami index is approximately equal with the space dimension, as it is predicted by theory of the instantaneous nucleation for the classical case [13, 14].

Table 2. Avrami index and logarithm of the crystallization rate constant as function of the dimensionality of the space.

Space dimension	Growth velocity	Avrami index	Error of the Avrami index	Intercept	Error of the Intercept
2.00	0.03	1.970	0.001	-8.632	0.005
3.00	0.10	2.953	0.002	-12.130	0.007
4.00	0.10	4.010	0.013	-18.600	0.053
5.00	0.30	4.986	0.025	-19.387	0.087
6.00	0.05	5.969	0.064	-21.370	0.190
7.00	0.05	6.956	0.061	-26.400	0.200
8.00	0.05	7.995	0.069	-31.511	0.233
9.00	0.05	8.982	0.069	-36.700	0.248
10.00	0.05	9.930	0.070	-41.700	0.258

The fact that the Avrami index is very close to the value predicted by the theory, shows that the Avrami equation has an universal behaviour.

We may also note that, as the dimensionality of the space increases, the error in the value of the Avrami index is slightly higher. This can be explained by the fact that the concentration of nuclei decreases as the dimensionality of the space increases, $g = \frac{s}{L^n}$.

The role of the concentration of nuclei may be further investigated by considering equation (7) that suggests a linear dependence of the crystallization rate constant on g . Therefore, we performed some sets of computer simulations in a 6-dimensional space for a hyper-cubic box with length $L = 5$, at a constant growth velocity $v = 0.05$, but at different nuclei concentrations. The obtained results are shown in Fig. 3.

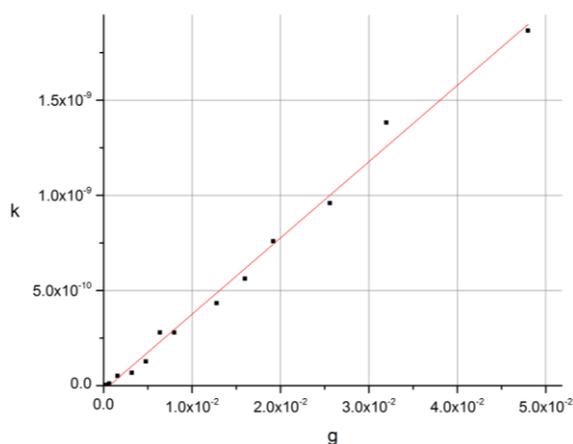


Fig. 3. Dependence of the crystallization rate as function of g for a cubic box with $L = 5$ and growth velocity $v = 0.05$ in a 7-dimensional space. The red line is the linear fit of the data.

The linear dependence of k versus concentration predicted by our equation (7) and verified by computer simulations is consistent with theoretical considerations in [13] and [14] for the usual 1D-3D spaces.

Furthermore, we also examined the role of the space dimensionality for the crystallization rate constant. In equation (7), this quantity appears at the exponent of the growth velocity.

We performed various computer simulations in the same 7-dimensional space in a hyper-cubic box with $L = 5$ at a constant concentration of nuclei $g = 1.92 \cdot 10^{-3}$ nuclei/unit of volume, but at different growth velocities.

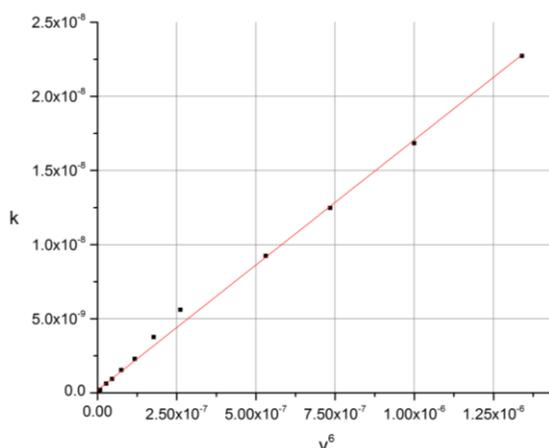


Fig. 4. Dependence of the crystallization rate as function of v^6 for a cubic box with $L = 5$ and concentration $g = 1.92 \cdot 10^{-3}$ nuclei/unit of volume in a 7-dimensional space. The red line is the linear fit of the data.

For a constant space dimension, the dependence of the crystallization rate on v^n (as predicted by equation (7)) is linear and this behaviour was obtained also by our computer simulations.

4. Conclusions

Polymer crystallization in a space having dimension larger than 3 has no "real" meaning so far, yet we wish to highlight that the Avrami equation has an universal behaviour, irrespective on the space dimensionality.

Since there are no means of experimentally verifying our theoretical predictions, in this manuscript we took the path of computer simulations. By means of Monte Carlo simulations, we studied the instantaneous nucleation mechanism of a hypothetical polymer situated in a multi-dimensional space. The results include the overall crystallization rate constant and the Avrami index for various conditions. The outcome was compared with the predictions from our generalized Avrami equation and we conclude that our computational model is in a very good agreement with the Avrami theory.

We adapted the classical KJMA method of instantaneous polymer crystallization to an n -dimensional space, obtaining the time dependence of the crystalline fraction of the material. We found that, even for a multi-dimensional space, the dependence obeys the classical Avrami equation. This means that the Avrami index is equal with the space dimension.

We also obtained the exact dependence of the crystallization rate constant on space dimension, growth velocity and nuclei concentration. The main conclusion of the study is that our equation is a generalization of the classical Avrami equation.

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