SPORADIC POLYMER CRYSTALLIZATION
IN THE n-DIMENSIONAL SPACE

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In this manuscript, we investigate the spontaneous polymer crystallization by extending the classical Kolmogorov–Johnson–Mehl–Avrami theory to a multi-dimensional space. We obtained a generalized Avrami equation, described by two parameters, the Avrami index and the overall crystallization rate constant, as the classical theory does. Both parameters essentially depend on the space dimensionality, and we confirm the results by means of computer simulations. We also investigated the dependence of the overall crystallization rate constant on the growing velocity and on the nucleation rate, expressed as number of nuclei that appear per unit time on the crystallization space. The simulation results are in very good agreement with our theoretical results, both of them also being direct generalizations of the prediction of the classical Avrami equation.

1. Introduction

The kinetics of crystallization of polymers is based on the formation and growth of crystalline regions which expand in the volume of the polymer during the process [1-6]. Both theoretical and experimental investigations of polymer crystallization process are based on the study of time evolution of the crystalline fraction for the material, X_c. This behaviour is based on the so called property of polymer semicrystallinity, that may be briefly explained as follows [1-4]: due to the very long polymer molecules, a number of monomers belonging to different macromolecules cannot enter in the crystalline state, remaining in the amorphous state. Therefore, the polymer is only semicrystalline and not completely crystalline. The crystalline fraction of the material is then the ratio between the volume of the crystallized region and the total material volume.

The polymer nucleation process is a two-step process: the first step consists in formation of the nuclei for the crystalline phase and the second consists in the growth of these centers [1-6]. If all the nucleation centers appear at the beginning of the nucleation, then this is called instantaneous nucleation, whereas, when the nuclei appear in the polymer volume at a constant time rate, the nucleation is called sporadic.

Irrespective of the nucleation mechanism type, the time evolution for the crystalline polymer fraction is described by the Avrami equation [1-6]. This equation has the origin on the probabilistic method of Kolmogorov [7] and it is based on the mean field approximation of Johnson and Mehl [8]. The expression of the Avrami equation is [1-6, 9-11]:

$$1 - X_c = exp(-kt^m) \tag{1}$$

with k being the overall crystallization rate constant and m - the Avrami index.

The form for this equation is the same, irrespective of the nucleation process type, but, in the case of the instantaneous nucleation, the Avrami index is equal with 3 and in the case of the

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sporadic nucleation this index is 4 (considering here a 3-dimensional space). The results of the model are in very good agreement with the experimental data [1-3, 12-14] and with the computer simulations [4-6]. The main conclusion of experimental and theoretical investigations of sporadic nucleation of polymers [1, 2], sustained as well by computer simulations, [4], consist in fact that the Avrami index is equal with space dimensionality plus one.

In a recent paper, we discussed the instantaneous polymer crystallization in a multi-dimensional space [15]. We extended the Kolmogorov–Johnson–Mehl–Avrami theory [7-11] to the instantaneous nucleation of polymers in a hypothetical multi-dimensional space, obtaining a generalized Avrami equation. We demonstrated that the Avrami index is equal to the space dimension, the same as for the classical case thoroughly discussed in [1, 2]. The theoretical results were confirmed by means of Monte Carlo simulations, and the obtained results were in very good agreement with the predictions. The main conclusion in [15] is that the Avrami equation describing the instantaneous nucleation has an universal behaviour, irrespective on the space dimensionality.

Additionally, this deduction is consistent with the results we obtained for polymer crystallization in frustrated conditions [6]. After a sufficient long time since the beginning of the crystallization, geometrical constraints determine the evolution of the process to be similar to a one in a space with reduced dimensionality.

The logical next step is to verify if this behavior is also valid for the sporadic nucleation in a n-dimensional space. In this manuscript, we present the theoretical approach for sporadic polymer nucleation in a multi-dimensional space, followed by computer simulations for verifying the results.

2. Molecular Model and Simulation Method

We start by deriving the expression of the coefficients for the Avrami equation in the case of sporadic nucleation in a n-dimensional space. As for instantaneous crystallization, recently described in [15], all hypotheses of the Avrami model are kept, yet adapted to the actual geometry of the space.

In the case of sporadic nucleation, the nuclei are formed at a constant time rate and are randomly and uniformly disposed in the volume of the sample. As soon as a nucleus is formed, it grows with constant rate [1, 2, 4]. We denote by I the number of nuclei that appear in the unit time per unit of volume and by v the (linear) growth velocity of the nuclei. The volume fraction of material which is still in the amorphous state is a generalized expression for the case of regular space [1, 2]:

$$1 - X_c = exp(-E) \qquad (2)$$

where E(t) is the average number of crystal fronts passing through a certain point P at the moment t:

$$dE(t) = \frac{n\,\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2}+1\right)} r^{n-1}\left(t - \frac{r}{v}\right) I dr \qquad (3)$$

where $dV_n = \frac{n\,\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2}+1\right)} r^{n-1} dr$ is the volume of a spherical hyper-shell situated at distance r from the origin, [16, 17] and $\Gamma(x)$ is the gamma function.

Because the linear velocity of the crystallization front is v, the average number of crystal fronts touching the point P in time t is [1, 2]:

$$E(t) = \int_0^{vt} dE(t) \qquad (4)$$

A straightforward, but tedious calculation gives:

$$E(t) = \frac{\pi^{\frac{n}{2}}}{(n+1)\Gamma\left(\frac{n}{2}+1\right)} I v^n t^{n+1} \qquad (5)$$

from where the expression in (2) may be rewritten:

$$1 - X_C = \exp\left(-\frac{\pi^{\frac{n}{2}}}{(n+1)\Gamma\left(\frac{n}{2}+1\right)} I v^n t^{n+1}\right) \qquad (7)$$

We have to note that the time dependence is t^{n+1}, whereas in the case of the classical Avrami theory for the 3-dimensional space, the time appears as t^4 [1, 2]. The coefficient of t^{n+1} is the generalized overall crystallization rate constant:

$$k = \frac{\pi^{\frac{n}{2}}}{(n+1)\Gamma\left(\frac{n}{2}+1\right)} I v^n \qquad (8)$$

As from [1, 2], the overall crystallization rate constant linearly depends on the number of nuclei which appear in the unit time per unit of volume and on the growth velocity to a power equal with the dimensionality of the space.

If $n = 3$, we obtain $k = \frac{\pi I v^3}{3}$, the classical value directly obtained for the 3-dimensional space [1, 2].

In order to obtain the Avrami index and crystallization rate constant, as usual, equation (5) is linearized by taking a double logarithm as in [1,2, 4-6, 15]

$$ln[-ln(1 - X_c)] = ln\,k + m\,ln\,t \qquad (9)$$

In this linearized form, $ln[-ln(1 - X_c)]$ depends on the first power of $ln\,t$ with the coefficient $m = n + 1$ being the Avrami index. As for classical calculation, the graph will be a line with the intercept being the logarithm of the crystallization rate constant.

3. Results and discussion

Previous theoretical considerations about sporadic nucleation in a multi-dimensional space were verified by means of Monte Carlo simulations. We used a specially revised computer simulation program, a modified version of the ones used in our previous works [4-6, 15].

In our Monte Carlo simulations, we consider the sporadic crystallization of a polymer in a hyper-cubic box of length L. At each time step during the run, a number I of nuclei are randomly and uniformly thrown inside the hyper-box. All the nuclei were uniformly grown with the same velocity v. We systematically recorded the volume percent of the crystalline fraction of polymer, X_c, calculated as the ratio between the volume occupied by hyper-spherulites and the volume of the hyper-cubic box. In the calculation of the volume fraction of the crystallized polymer, we discarded spherullites overlapping as we did in our previous simulations, [4-6, 15].

To check our theoretical considerations, we made computer simulations for a wide range of multi-dimensional spaces, spanning between 2 and 10 dimensions. The simulations were performed in a hyper-cubic box with length $L = 5$, $I = 5\,\frac{nuclei}{unit\ of\ time}$ and the results are depicted in table 1.

Table 1. Avrami index and logarithm of the crystallization rate constant at different space dimensionalities.

Space dimension	Growth velocity	Avrami index	Error of the Avrami index	Intercept	Error of the Intercept
2	0.005	3.023	0.002	-11.113	0.008
3	0.010	3.997	0.020	-15.691	0.067
4	0.010	5.022	0.015	-22.037	0.061
5	0.010	5.996	0.017	-28.164	0.069
6	0.050	7.015	0.037	-25.200	0.113
7	0.050	7.961	0.049	-29.900	0.158
8	0.050	8.946	0.081	-34.800	0.275
9	0.050	9.850	0.052	-39.600	0.182
10	0.050	10.880	0.094	-45.000	0.353

With very good approximation, we obtained that the Avrami index is equal with the space dimension plus one, as it is predicted by equations (7) and (9) and how theory of the spontaneous nucleation for the 3-dimensional space forsees [1, 2, 13, 14].

As we noted for the instantaneous nucleation in [15], we may observe that the error of the Avrami index increases as the dimension of the space increases. The explanation of this behaviour is as before: as the space dimensionality increases, the nuclei concentration decreases as L^{-n}, and the errors in determining the concentration become significant.

The main conclusion of this set of runs is that the Avrami equation in the case of the sporadic nucleation has an universal behaviour. For the sake of completion, we present in Figure 1 the time evolution of the crystalline fraction of the material for a hyper-cubic box with length $L = 5$ in a 5-dimensional space, at a growing nuclei velocity $v = 0.010$ and with the number of nuclei per unit time $I = 5$.
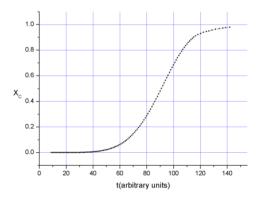

Fig. 1: Sporadic crystallization in a 5-dimensional space. Volume fraction of the crystallized polymer as function of time for a cubic box with L = 5, growth velocity v = 0.010 and number of nuclei per unit volume I = 5.

The time behaviour of the volume fraction of the crystalized polymer is similar with the behaviour in the usual 3-dimensional space. Because of the relatively small growth velocity and number of nuclei per unit of volume, for a long period of time at the beginning of the run, the fraction is quite small.

The graph in Figure 2 is the linearized representation of data in figure 2 and it illustrates the way of extraction of the Avrami index and logarithm of the crystallization rate constant by linear fitting the simulated results.
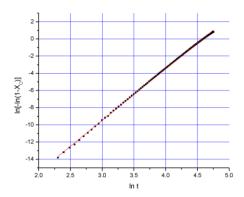

Fig. 2: Sporadic crystallization in a 5-dimensional space. Linearization of data from figure 1.

The linear fit of the simulated data gives $m = 5.996 \pm 0.017$ and $\ln k = -28.164 \pm 0.069$, result also depicted in the Table 1. We again point out that the Avrami constant is the space dimensionality plus one, *i.e.*, for the our considered example, $m = 5 + 1$.

Furthermore, we investigate the influence of the space dimensionality on the overall crystallization rate constant obtained in equation (8). Accordingly, k depends linearly on v^n. Therefore, we made several computer simulations for a hyper-cubic box with length $L = 5$ situated in a 5-dimensional space. In all simulations, the number of nuclei per unit time was time $I = 5$, and the growth velocity was between 0.008 and 0.1. The results are shown in figure 3 and illustrate the theoretical expectation on linear dependency of k to v^n.

We repeated the procedure for other space dimensions, finding that the illustrated dependence is preserved. The behaviour is consistent with classical theoretical calculations for the sporadic nucleation [1-3] and with other computer simulations [4].
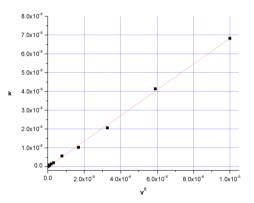

Fig. 3. Dependence of the overall crystallization rate constant as function of v^5 for a cubic box with $L = 5$ and $I = 5$ nuclei/unit time in a 5-dimensional space. The red line is the linear fit of the data.

In addition, equation (8) predicts that overall crystallization rate constant linearly depends on the number of nuclei per unit time. We checked this by Monte Carlo simulations, employing a hyper-cubic box with length $L = 5$ situated in a 5-dimensional space, at a growth velocity $v = 5$.

From figure 4, one may observe that linear dependence between k and I is reasonable obtained, being in accordance with both theoretical predictions and computer simulations for the classical case [1, 2, 5].
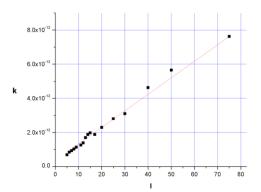
Fig. 4. Dependence of the crystallization rate as function of I for a cubic box with $L = 5$ and growth velocity $v = 5$ in a 5-dimensional space. The red line is the linear fit of the data.

We remark that, as the number of nuclei per time unit increases, the results in figure 4 become slightly imprecise, due to the fact that the simulation space is too fast filled with nuclei and the precision of determination of the crystallized fraction is poor.

4. Conclusions

In the present paper, we investigated sporadic polymer crystallization in a hypothetical multi-dimensional space, both theoretical and by computer simulations. We adapted the now classical Kolmogorov–Johnson–Mehl–Avrami theory of sporadic nucleation of polymers to spaces with dimensions higher than 3, obtaining the time dependence of the crystalline fraction of the material. Our results are a generalization of the classical Avrami equation which provides the overall crystallization rate constant and the Avrami index. The most important parameter, the Avrami, index is equal with the space dimensionality, plus one, in agreement with the value of 4 in the classical Avrami theory (for a 3 dimensional case).

The theoretical predictions were verified by means of Monte Carlo computer simulations. From the simulation data, we calculated the overall crystallization rate constant and the Avrami index. The simulation results were in very good agreement with the calculations.

Employing computer simulations, we also systematically investigated the dependence of the overall crystallization rate constant on the crystallization velocity. We found that the dependence is linear on v^n, as it is calculated from our theory. The result is in perfect agreement with the classical Avrami theory.

Another check for the validity of the theoretical results was done by the verification of the overall crystallization rate constant dependence on the nuclei number per unit time. Again, both theoretical and simulated results were in perfect agreement with classical theory.

The main conclusion of this paper, along with the conclusion of our previous work in [15] devoted to the instantaneous polymer crystallization, is that, regardless on the space dimensionality, the Avrami equation has an universal behaviour.

References

[1] R. A. Pethrick, Polymer Structure Characterization. From Nano to Macro Organization, The Royal Society of Chemistry, Cambridge (2007).

[2] U. W. Gedde, Polymer Physics, Chapman & Hall, London (1995).

[3] G. Reiter, G. R. Strobl (Eds.), Progress in Understanding of Polymer Crystallization, Springer Verlag Berlin (2007).

[4] C. Berlic, V. Barna, B. Manolescu, D. Dena, Digest Journal of Nanomaterials and Biostructures **8**(4), 1845 (2013).

[5] C. Berlic, V. Barna, B. Manolescu, D. Dena, Digest Journal of Nanomaterials and Biostructures **9**(1), 197 (2014).

[6] C. Berlic, V. Barna, B. Manolescu, B. Mahler, D. Staicu, Digest Journal of Nanomaterials and Biostructures **9**(3), 919 (2014).

[7] A.N. Kolmogorov, Bull. Acad. Sci., USSR Ser. Math. **3**, 355 (1937).

[8] W.A. Johnson, R.F. Mehl, Trans. Metall. Soc. AIME, **135**, 416 (1939).

[9] M. Avrami, J. Chem. Phys., **7**, 1103 (1939).

[10] M. Avrami, J. Chem. Phys., **8**, 212 (1940).

[11] M. Avrami, J. Chem. Phys., **9**, 177 (1941).

[12] H. Janeschitz-Kriegl, Crystallization Modalities in Polymer Melt Processing. Fundamental Aspects of Structure Formation, Springer-Verlag Wien (2010).

[13] G. Allegra (Ed.), Interphases and Mesophases in Polymer Crystallization I, in Advances in Polymer Science, **180**, Springer Verlag (2005).

[14] G. Allegra (Ed.), Interphases and Mesophases in Polymer Crystallization II, in Advances in Polymer Science, **181**, Springer Verlag (2005).

[15] C. Berlic, V. Barna, B. Manolescu, Digest Journal of Nanomaterials and Biostructures, **10**(4), 1365 (2015).

[16] J.R. Weeks, The Shape of Space: How to Visualize Surfaces and Three-Dimensional Manifolds (Monographs and Textbooks in Pure and Applied Mathematics), **96**, Dekker (1985).

[17] G. E. Andrews, R. Askey, R. Roy, Encyclopedia of Mathematics and its Applications: Special Functions, Cambridge University Press (2001)