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INVESTIGATIONS ON THE NUCLEATION PROCESSES IN FRUSTRATED POLYMERIC SYSTEMS

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By means of Monte Carlo simulations, we investigated the nucleation of polymers in frustrated spaces, *i.e.* in spaces where one dimension is much smaller (or larger) than other (or others). The obtained results were compared with those predicted by the Avrami equation. In the case of the spontaneous nucleation, we found similarities with respect to the ordinary crystallization case, but the Avrami index has smaller values. For instantaneous nucleation conditions, we observed to have two distinctive regimes: 3-dimensional crystallization at the beginning of the process, followed by a behavior which is similar with the one that occur in spaces with low dimensionalities.

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1. Introduction

By means of Monte Carlo simulations, we recently investigated the nucleation of polymeric materials and we compared these results with those obtained from the Avrami equation [1, 2]. In the first paper, we studied sporadic nucleation [1], while in the second we considered the spontaneous one [2].

The classical way of investigating the crystallization process of polymers consists in the examination of evolution of the crystalline fraction of the material, X_c [1-8] and the analysis of the results is done using the Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [9-13]. The KJMA theory expresses X_c in the form of the Avrami equation [1-3, 7]:

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

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

In the case of the sporadic nucleation, the crystallization nuclei appear at a constant rate and are uniform disposed in the volume of the probe [1,3,7,14]. After formation, they grow at constant rate. The value of the Avrami index is [1,18]:

$$n = n_d + n_n \tag{2}$$

where n_d represents the dimensionality of the growing crystals and $n_n = 1$ represents the time dependence of the nucleation. The overall crystallization rate constant is

$$k = \frac{\pi I v^3}{3} \tag{3}$$

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with *I* being the number of nuclei which appear in the unit time per unit of volume and v the growth velocity of the nuclei.

In the case of the instantaneous nucleation, all the nuclei are formed at the beginning of the crystallization and start to spherically grow at constant rate [2,3,7,14]. In this situation, $n = n_d$, which, in this case, is equal with the dimensionality of the space. The overall crystallization rate constant is

$$k = -\frac{4}{3}\pi v^3 g \tag{4}$$

where g is the is the number of nuclei per unit volume and v is again the growth velocity of the nuclei.

Our preceding efforts were devoted to obtain computer programs capable to simulate the sporadic [1] and instantaneous [2] nucleation of polymeric materials. From our data, we calculated the overall crystallization rate constant and the Avrami index. The obtained results were in excellent agreement with theoretical prediction of the Avrami equation (1) for both types of nucleation mechanisms.

In both cases, we also checked the dependence of the overall crystallization rate constant on the growth velocity, finding the laws predicted by equations (3) and (4).

Motivated by these interesting previous results, we shift our attention towards another attractive situation i.e. when the crystallization it is not completely free, but it is geometrically hindered, as in frustrated systems

In the acception of this paper, a frustrated system is a system where one dimension is much smaller (or larger) than other (or others). For instance, the cubic simulation box from [1] and [2] is transformed here is a L*x*L*x*H rectangular box. If $L \ll H$, we can consider a crystallization in a thin rod-like cavity (similar to a nanotube, for example), while, if $H \ll L$, we have crystallization in a thin film.

2. Molecular Model and Simulation Method

Firstly, we investigated the instantaneous nucleation of a frustrated system. As we described in [2], in order to simulate this kind of nucleation, at the beginning of the run, we randomly throw all the crystallization nuclei inside the volume of the box. All the nuclei were spherically grown with the same velocity, v.

By theoretical point of view, we considered that crystallization in the frustrated systems takes place in the same conditions as in the bulk space [1-9], except the frustration upon one or two dimensions, as in Figure 1.

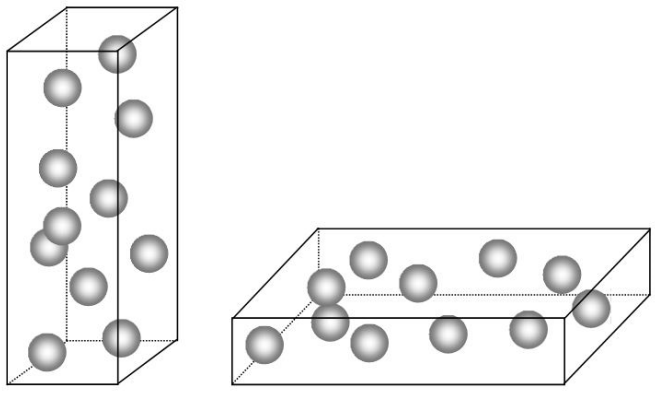

Fig. 1. Instantaneous nucleation in a frustrated system.a. Nucleation in a thin rod-like cavity (similar to a 1D case). b. Nucleation in a thin film (similar to a 2D case).

During the simulation, we recorded the volume percent of the crystalline fraction of polymer, X_c, calculated as the ratio between the volume occupied by spherulites (taking account of overlapping) and the total volume of the rectangular box.

The characterization of the crystallization process is done by obtaining from simulated data the overall crystallization rate constant, k, and the Avrami index, n. These quantities may be directly determined using methods similar to those from [15] and [16], but, usually, the parameters are obtained by taking the double logarithm in the Avrami equation (1) [1-8]:

$$ln[-ln(1-X_c)] = ln\,k + n\,ln\,t \tag{5}$$

If we draw the graph the left side in the above equation as function of $\ln t$, we obtain a line with the slope equal with the Avrami index, and the intercept equals the logarithm of the crystallization rate constant.

3. Results and discussion

The first set of simulations were performed in a rectangular box with length $L = 2$ and height $H = 200$, i.e. comparable to the shape of a thin rod-like cavity. The nucleation was instantaneous, thus, at the beginning of the simulation, we threw a number of nuclei $s = 50$ (resulting a number of nuclei per unit volume $g = 0.0625$). The growing velocity was $v = 0.015$. The dependence of the volume fraction of the polymer as function of time is depicted in Fig 2.

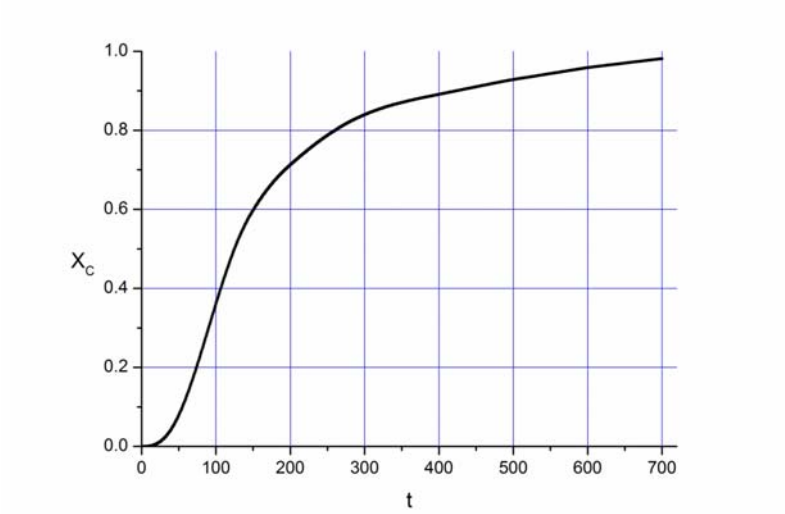

Fig. 2: Volume fraction as function of time for a rectangular box with $L = 2$, $H = 200$ *and* growth velocity $v = 0.015$.

The sigmoid behavior of this curve has similarities with the theoretical [3,7] and with the simulated one [2], but its shape is quite distorted, especially in its final part.

For calculating the parameters of the Avrami equation, we tried to use the linearized form (5) of this equation, as is usually done [1-8]. Instead of finding a linear dependence of $ln[-ln(1-X_c)]$ as function of $ln\,t$, we found two connected lines, as in figure 3.

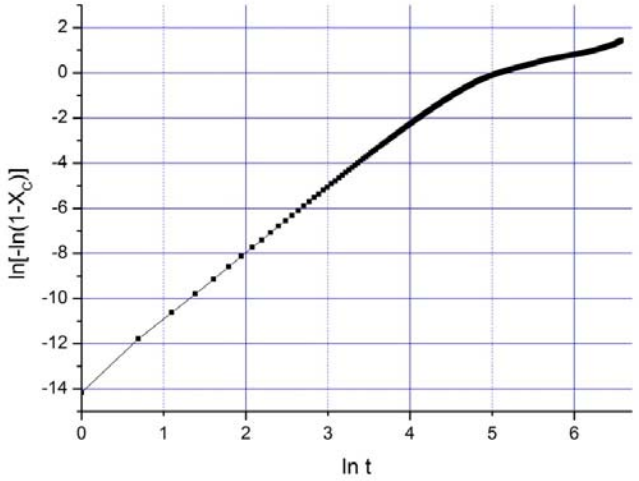

Fig. 3: Representation of the equation (5) for a rectangular box with $L = 2,\ H = 200$ *and* growth velocity $v = 0.015$. *The lines are guide for the eyes.*

In order to elucidate the behavior from Figure 3, we separately studied the two regions.

In Fig 4, we show the graph of the first part for the plot from figure 3, along with its linear fit. We found that, for this portion, the Avrami index is $n = 3.003 \pm 0.023$ and $ln\, k = -13.994 \pm 0.047$.

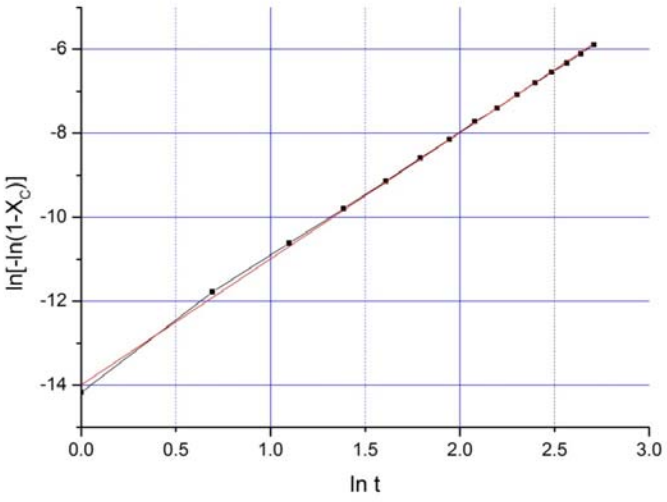

Fig. 4: Plot of the first part of the graph from Figure 3. The red line is the linear fit of data.

Fig. 5 represents the plot of the points after the curvature of the graph from figure 3. The draw is again a line, so we made its linear fit, finding the Avrami index $n = 1.004 \pm 0.003$ and $ln\, k = -5.105 \pm 0.016$.

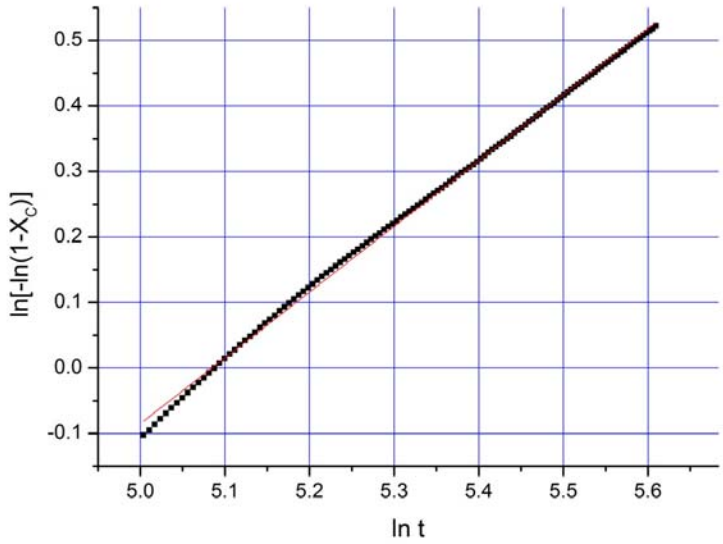

Fig. 5: Plot of the second part of the graph from Figure 3. The red line is the linear fit of data.

Remembering that we deal with an instantaneous nucleation and the simulation box is heavily asymmetric, $L = 2$ and $H = 200$, these values of the Avrami indexes may be explained as follows:

At the beginning of the simulations, all the nuclei are very small, even in comparison with the smallest dimension of the simulation box, so the growing is 3-dimensional, with $n \cong 3$. After the nuclei have grown enough, their dimensions become important comparative with the smallest dimension of the simulation box. In our situation, the only direction where the nuclei may still grow is along the height of the box, so the nucleation become 1-dimensional, with $n \cong 1$. In the last part, the graph from figure 3 it is not linear. We explain this behavior by the fact that, despite the fact the growing space is very asymmetrical, the growth velocity has a spherical profile.

The simulation of the instantaneous nucleation was also done for a thin film, represented as a rectangular box with dimensions $L = 200$ and $H = 5$, having $s = 50$ growing nuclei (resulting a number of nuclei per unit volume $g = 5 \cdot 10^{-4}$). The grow velocity was $v = 0.015$. The plot of the quantity $ln[-ln(1 - X_c)]$ as function of $ln\, t$, is similar with that from Figure 3, resulting again two linear regions. Linear fit of the first region gives the Avrami index $n = 3.006 \pm 0.012$ and $ln\, k = -15.236 \pm 0.031$, while the fit for the second ones gives $n = 2.000 \pm 0.004$ and $ln\, k = -10.999 \pm 0.025$. The explanation for this behavior is somehow similar to the previous situation. At the beginning of the simulation, the system behaves 3-dimensional. The nuclei then grow in time and, after a certain point, the simulation becomes 2-dimensional, since, in this case, we only have one dimension that is much smaller than the other two.

We investigate the role of the growing velocity by repeating the simulations for the same simulation boxes and for the same number of growing nuclei. The summaries of the acquired data are presented in Tables 1 and 2.

Table 1. Avrami index and logarithm of nucleation rate as function of nuclei growth velocity for a rectangular box with with $L = 2,\ H = 200$.

No.	v	n_1	n_1 error	n_2	n_2 error	ln k_1	ln k_1 error	ln k_2	ln k_2 error
1	0.07	2.915	0.016	1.086	0.007	-9.333	0.024	-3.627	0.030
2	0.06	2.918	0.008	0.996	0.002	-9.773	0.014	-3.808	0.009
3	0.05	2.923	0.010	1.144	0.000	-10.302	0.018	-4.402	0.003
4	0.04	2.941	0.005	1.055	0.005	-10.980	0.009	-4.421	0.030
5	0.03	2.982	0.013	1.037	0.005	-11.909	0.022	-4.487	0.025
6	0.02	3.001	0.023	1.102	0.001	-13.141	0.044	-5.169	0.006
7	0.01	3.003	0.013	1.107	0.001	-15.236	0.032	-5.839	0.007

Table 2. Avrami index and logarithm of nucleation rate as function of nuclei growth velocity for a rectangular box with with $L = 200,\ H = 5$.

No.	v	n_1	n_1 error	n_2	n_2 error	ln k_1	ln k_1 error	ln k_2	ln k_2 error
1	0.07	2.995	0.011	1.992	0.001	-14.172	0.019	-10.173	0.009
2	0.06	3.004	0.018	2.050	0.003	-14.710	0.051	-10.782	0.022
3	0.05	3.006	0.012	2.000	0.004	-15.236	0.031	-10.999	0.025
4	0.04	3.052	0.041	2.000	0.002	-15.928	0.072	-11.335	0.012
5	0.03	3.021	0.010	2.000	0.003	-16.799	0.028	-11.900	0.021
6	0.02	2.991	0.009	1.968	0.000	-17.916	0.028	-12.597	0.003
7	0.01	2.982	0.014	2.000	0.000	-19.948	0.048	-14.129	0.006

The above tables show that, for both types of simulation boxes, the behavior of the frustrated system is the same: at the beginning of the nucleation process, we have a 3-dimensional nucleation which finally evolves in a 1-dimensional or 2-dimensional one, depending on the geometry of the growing space. As the nuclei radius increases with time, the reduction of the space dimensionality due to the frustration hinders the growth of the nuclei and the dimensionality of the space is decreased by one or two, respectively.

Using the values from table 1 and table 2, we present the graph of crystallization rate as function of v^3, for the first part of the nucleation process. We found a linear dependence as in Figure 6 and 7, as it is predicted from equation (4) for the coefficient k of the Avrami equation.

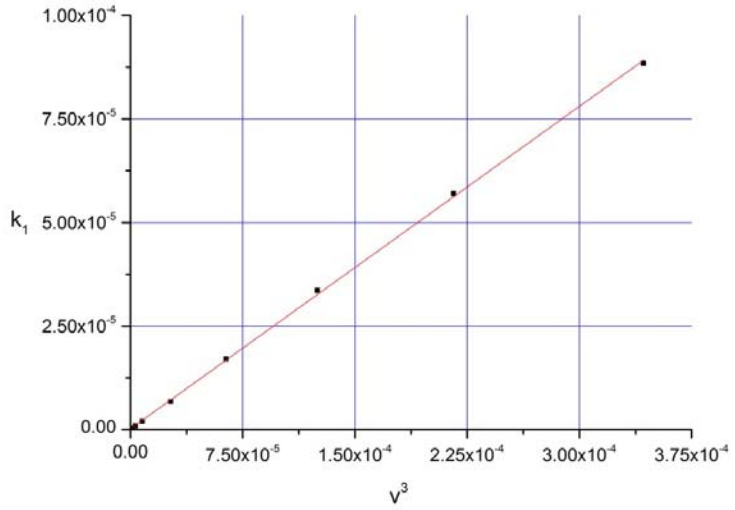

Fig. 6: Dependence of crystallization rate as function of v^3 for rectangular box with $L = 2$ and $H = 200$ The red line is the linear fit of data.

The linear fit of k_1 as function of v^3 gives a line passing through origin, as is predicted from (4). The slope of the line is 0.2595 ± 0.0019. From this value, we may calculate the number of nuclei per unit volume as $g = 0.0621$. This value is in excellent agreement with the starting value of g, as it is obtained from initial parameters of the simulation: $g = \frac{s}{L^2 H} = \frac{50}{800} = 0.0625$.

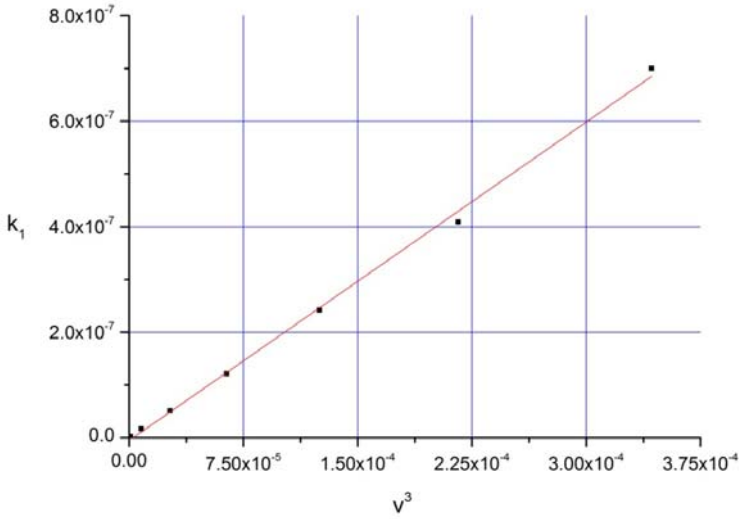

Fig. 7: Dependence of crystallization rate as function of v^3 for rectangular box with $L = 200$ and $H = 5$ The red line is the linear fit of data.

For the thin film, the same calculation as before, but using data from Fig. 7, gives the number of nuclei per unit volume, $g = 4.8 \cdot 10^{-4}$, while the value settled from the parameters of the simulation is $g = 5.0 \cdot 10^{-4}$. Again, the agreement between these parameters is very good.

This verification process of the linear dependence between crystallization rate and the third power of the grow velocity leads us to the conclusion that our hypothesis is correct: at the beginning of the simulation, the system behaves 3-dimensional, irrespective of the frustration type.

We also apply the above consideration for the second part of the graph from Figure 3, when the dimensionality is reduced by one unit. For the rectangular box with dimensions L = 2 and H = 200 (shape of a thin rod-like cavity), we found that k_2 depends approximately linear on v, as we expect from transcribing equation (4) for a 1-dimensional space. In the same time, we found that for the box with dimensions $L = 200$ and $H = 5$ (thin film-like shape), k_2 depends approximately linear on v^2, as it is expected for crystallization in a 2-dimensional space.

We also investigate the sporadic nucleation in frustrated spaces. In Figure 8, we present the dependence of the volume fraction of the polymer as function of time for a rectangular box with L = 2 , H = 200 and growth velocity v = 0.01.

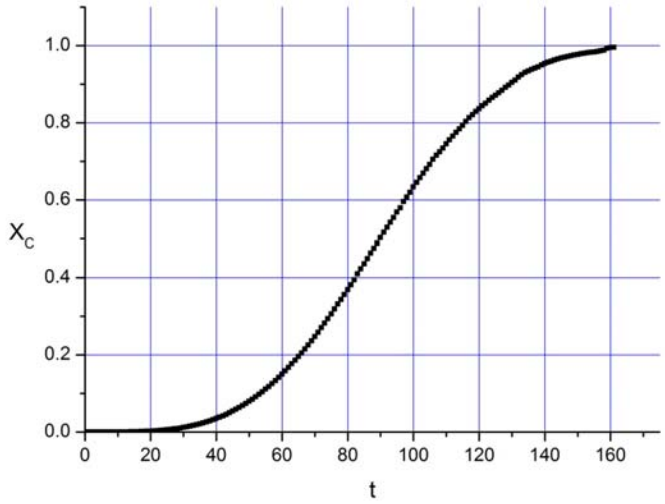

Fig. 8: Volume fraction as function of time for a rectangular box with $L = 2$, $H = 200$ *and* growth velocity $v = 0.01$.

One may notice that the shape of the graph is more symmetrical, compared with the corresponding one from figure 2, having much similarities with those predicted by theory and also founded in [1] and [2]. For calculating the parameters of the Avrami equation, we again use the linearized form (5) of this equation. The dependence of $ln[-ln(1 - X_c)]$ as function of $ln\, t$ is linear, as it may be noticed from Figure 9:

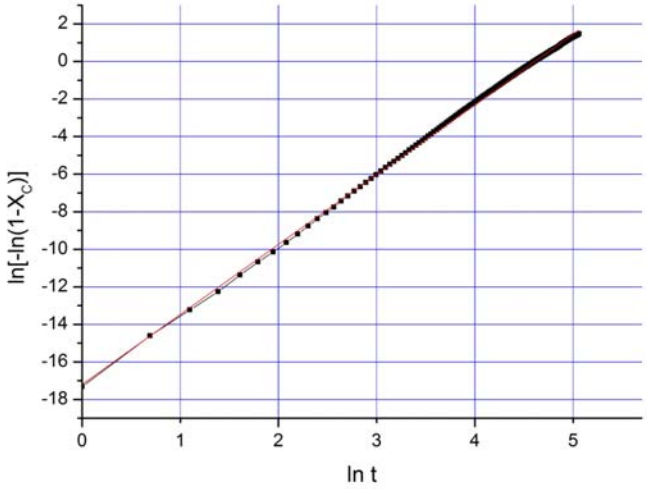

Fig. 9: Representation of the equation (5) for a rectangular box with $L = 2$, $H = 200$ *and* growth velocity $v = 0.01$.
The red line represents the linear fit of the data.

The main difference between instantaneous and sporadic nucleation in frustrated spaces is that for the latest we have only one kinetic region, as it is expected from the classical Avrami theory, while for the first, our simulation predict that we have two distinct regimes. In our opinion, the explication for this behavior consists in the fact that, for the sporadic nucleation, the new nuclei appear all over the simulation and their growth is approximately 3-dimensional, because they start from very small dimensions.

We verified this assertion by performing Monte Carlo simulations for both thin rod-like cavity and thin film-like shapes. We found that the value of the Avrami index is close to value 4, as it is expected for the 3-dimensional sporadic nucleation [1,3,7], but the values are slightly smaller than those obtained in [1]. The results are summarized in table 3.

Table 3. Avrami index and logarithm of nucleation rate as function of nuclei growth velocity for different types of rectangular boxes.

L	H	N	V	No nuclei	n1	n1 error	ln k1	ln k1 error
Thin rod-like cavity								
2	200	50	0.07	50	3.797	0.020	-11.995	0.042
			0.06	50	3.832	0.015	-12.521	0.032
			0.05	50	3.873	0.008	-13.058	0.016
			0.04	50	3.848	0.008	-13.655	0.019
			0.03	50	3.942	0.017	-14.696	0.038
			0.02	50	3.931	0.027	-15.821	0.066
			0.01	50	3.953	0.013	-17.876	0.034
Thin film								
200	5	100	0.07	100	3.758	0.017	-17.152	0.069
			0.06	100	3.759	0.012	-17.550	0.048
			0.05	100	3.758	0.009	-18.044	0.037
			0.04	100	3.727	0.010	-18.586	0.048
			0.03	100	3.712	0.010	-19.292	0.051
			0.02	100	3.749	0.006	-20.528	0.032
			0.01	100	3.803	0.003	-22.700	0.020

4. Conclusions

Using Monte Carlo simulations, we studied the crystallization processes in frustrated systems, *i.e.* a space with one dimension much smaller (or larger) than other (or others). The application of the simulated results may be applied to crystallization of thin polymeric films or for polymer chains confined in rod-like cavities.

For the sporadic nucleation, the results have many similarities with those obtained earlier for regular spaces, but the resulting Avrami index has somewhat lower values.

However, the central point is represented by the instantaneous nucleation case, where we find two individual regimes: one 3-dimensional crystallization at the beginning of the process and, for the later stage, a behavior similar to one that occurs in spaces with low dimensionalities (1-dimensional for the thin rod-like cavity and 2-dimensional for the thin film like systems).

We also checked our results by calculating from simulation the number of nuclei per unit volume and comparing them with those established by simulation parameters. The results were in very good agreement.

These two different behaviors can be explained by taking into account that at the beginning of the simulation, the nuclei are sufficiently small to not be aware of the reduced dimensionality of the space. As the nuclei increase in time, the reduction of the space dimensionality due to the frustration hinders their growth and the dimensionality of the space is decreased by one or two respectively.

In the case of sporadic nucleation, because the nuclei constantly materialize during the whole simulation process, we always have the situation when some nuclei are very small compared to the space frustration (subsequently, the process always retain some 3-dimensional characteristic).

The main conclusion is that the universality of the Avrami equation is preserved, even for situations when the space is not perfectly homogeneous, and it may well describe also some atypical crystallization processes.

Acknowledgements

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