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STUDY OF THE INSTANTANEOUS NUCLEATION PHENOMENA IN SOFT MATTER SYSTEMS BY MEANS OF MONTE CARLO SIMULATION

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In this paper, we investigate the process of phase transformation in polymeric materials by imposing instantaneous nucleation conditions in the employed Monte Carlo type simulations. We calculated the overall crystallization rate constants and the Avrami indices for various simulation circumstances and the obtained results were equivalent with those predicted by the Avrami equation. The dependence of the crystallization rate constant on the growth velocity and concentration of the nuclei was also investigated and a comparison was made with the already existing theory.

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1. Introduction

Recently, by using Monte Carlo simulations, we investigated the sporadic nucleation of polymeric materials and we compared these results with those obtained from the Avrami equation [1]. As it is thoroughly explained in literature [1-7], the kinetics of crystallization of polymers is based on the appearance and growth of the crystalline regions which emerge and expand in the volume of the polymer.

The theoretical and experimental macroscopic studies of the crystallization process are mainly based on the recording the evolution of the crystalline fraction of the material, X_c (*i.e.* the ratio between the volume of the crystallized region and the total volume of the material), as function of the time [1-7].

From our recorded data obtained for the sporadic nucleation, we calculated the overall crystallization rate constant and the Avrami index [1]. The simulations were carried out for usual 3-Dimensional space, but also for 2-Dimensional and 1-Dimensional spaces, the results being in excellent agreement with theoretical prediction of the Avrami equation for the type of the studied nucleation.

In computer simulations for the 3-Dimensional space, we also systematically investigated the dependence of the overall crystallization rate constant on the crystallization velocity. For the 3-D space, we found that the dependence of this parameter is on the 3-rd power of v, as is predicted from theory [6, 7].

These previous results gave us a solid image about the versatility of the Avrami model in the investigation of the sporadic nucleation in soft matter systems. One may put the question if the simulated results still remain in good agreement with the theory when employing the instantaneous nucleation mechanism.

In order to gain further understandings in this direction, we present in the current paper the results of Monte Carlo type computer simulations using the method of instantaneous nucleation.

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2. Molecular Model and Simulation Method

As we described in [1], the method of analyzing the phase transformation of polymers is the Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [8-12].

As soft matter systems, polymers generally crystallizes by two mechanisms [6,7]:

1. instantaneous nucleation, also called athermal nucleation: all the nuclei are formed at the beginning of the crystallization and start to spherically grow at constant rate;
2. sporadic nucleation, also called thermal 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. This was the mechanism investigated in [1].

In this work, we were interested in the athermal nucleation, thus we will present here its main hypothesis and aspects [6, 7].

At the beginning of the crystallization process, $t = 0$, all the nuclei randomly appear and begin to spherically grow with a constant velocity v. In follows that, at any time instance, all the spherulites have the same radius.

As for sporadic nucleation, this approach also permits that two growing nuclei mutually invade each other. The mechanism is schematically illustrated in Figure 1.

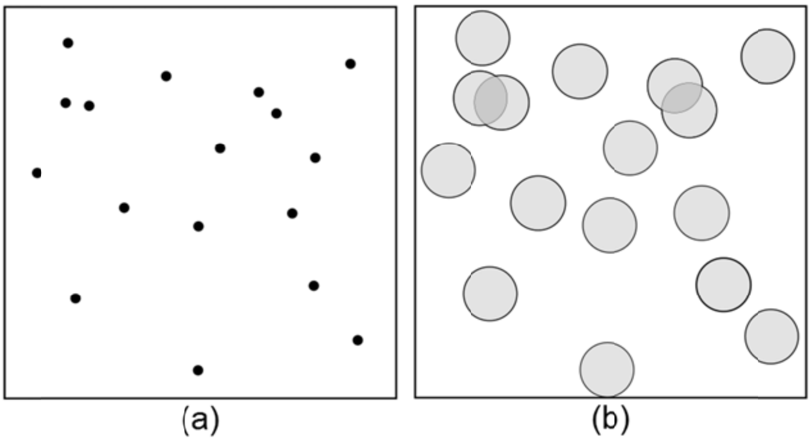

Fig. 1: Mechanism of the instantaneous nucleation.
a. Initial stage of the nucleation. At $t = 0$, all the nuclei appear in the bulk.
b. Growth of the nuclei. For all $t > 0$, the nuclei have the same radius.

As for sporadic nucleation, statistical analysis of the instantaneous crystal growth may be seen in terms of an expanding circular wave front [6, 7], described by Poisson distribution:

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

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

Since all the spherulites grow with same velocity, the average number of crystal fronts passing through point P at the moment t is [6, 7]:

$$E(t) = \frac{4}{3}\pi(vt)^3 g \tag{2}$$

where g is the number of nuclei per unit volume.

$P(0)$ is the probability that the point P has not been touched yet by a wavefront, so it may be seen as the volume fraction of the polymer which is still in the molten state:

$$P(0) = 1 - X_c \tag{3}$$

with X_c the crystalline fraction of the material.

Combining equations (1), (2) and (3), we obtain [6, 7]:

$$1 - X_c = exp\left(-\frac{4}{3}\pi v^3 g\, t^3\right) \tag{4}$$

The above equation is usually written in the Avrami form [1-7]:

$$1 - X_c = exp(-kt^n) \tag{5}$$

where: $k = -\frac{4}{3}\pi v^3 g$ is the overall crystallization rate constant which depends on the third power of the growth velocity and linear on the number of nuclei per unit volume.
n is the Avrami index, that, for instantaneous nucleation, is equal with the dimensionality of the space, [6,7].

In order to describe the crystallization process in soft matter systems, it is necessary to obtain from measured or simulated data the overall crystallization rate constant, k, and the Avrami index, n. Using methods similar to those from [13, 14], they could be directly determined, but, usually, the Avrami equation is linearized by taking the double logarithm in equation (5) [1-7]:

$$ln[-\,ln(1 - X_c)] = ln\, k + n\, ln\, t \tag{6}$$

It this case, a line is obtained having the slope equal with the Avrami index, while the intercept equals with the logarithm of the crystallization rate constant..

In our Monte Carlo simulations, we consider the instantaneous nucleation of a polymer in a cubic box of length L, the programs being modified versions of those used in [1]. At the beginning of the run, we randomly threw all the nuclei inside the volume of the box. At all subsequent moments of time, the nuclei were spherically grown with the same velocity, v. At every time step during the simulation, we recorded the volume percent of the crystalline fraction of polymer, X_c. This quantity was calculated as the ratio between the volume occupied by spherulites (taking account of overlapping) and the total volume of the box.

3. Results and discussion

We present here a set of simulation results obtained for a cubic box with length $L = 5$, at a growing nuclei velocity $v = 0.005$ and with the number of nuclei $s = 2000$ (resulting a number of nuclei per unit volume $g = 16$). The dependence of the volume fraction of the crystallized polymer as function of time is depicted in Fig. 2. The shape of the graph is identical with the theoretical one predicted in [6, 7] on the basis of the Avrami equation (4) and is similar with those obtained in [1] in the case of sporadic nucleation.

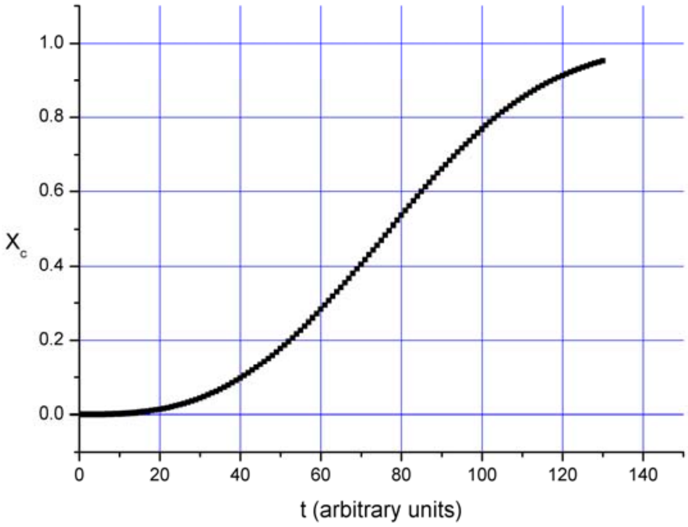

Fig. 2: Volume fraction of the polymer as function of time for a cubic box with $L = 5$, growth velocity $v = 0.005$ *and concentration of the nuclei* $g = 16$.

At this point, we have to notice the same drawback as for sporadic nucleation: the simulation results based on the Avrami equation (4) predict a final volume fraction of the crystallized phase tending towards 1. As already mentioned in [1], the polymers are semicrystalline, because the crystals are never completely filling the volume and the degree of crystallinity is never equal to 1. This discrepancy was explained by the simplifications of the Avrami model and by the observation that the real nucleation of a polymer is a mixture of athermal and thermal nucleation.

In order to calculate the Avrami index and the crystallization rate constant, we used the linearized form (6) of the Avrami equation. In the left side of this equation, there is a double logarithm depending on the volume fraction of the crystallized phase, while in the right side there is a line equation having the slope equal to the Avrami index. The intercept is represented by the logarithm of the crystallization rate constant. The graph in Figure 3 is the linearized representation of the data from Figure 2.

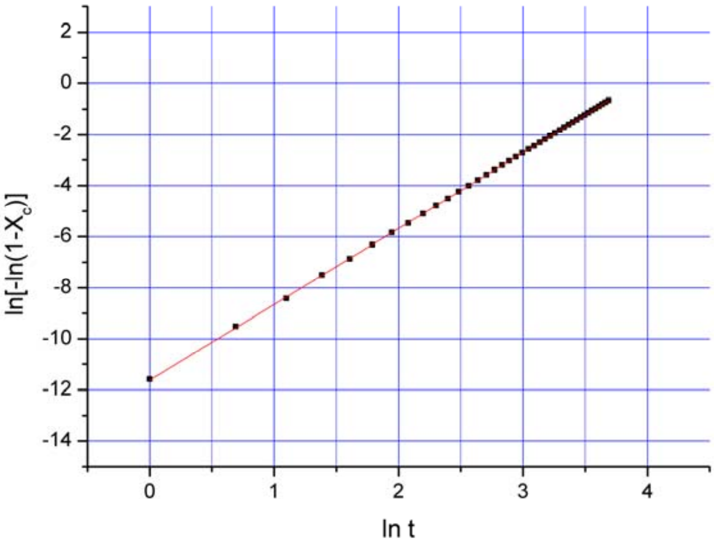

Fig. 3: Representation of the equation (6) for a cubic box with $L = 5$, growth velocity $v = 0.005$ *and concentration of the nuclei* $g = 16$. *The red line represents the linear fit of the data.*

The linear fit of our simulated data gives $n = 2.971 \pm 0.002$ and $ln\, k = -11.628 \pm 0.008$ which are results in very good agreement with the values predicted in [6, 7] for 3-Dimensional space.

Crystallization in a soft matter system, in particular of polymers, irrespective of the fact that the process is a sporadic or a instantaneous one, critically depends on the growth velocity of the nuclei. This may be observed from equation (4) and is thoroughly discussed in [2-7]. In our computer simulations, the role of this important parameter was investigated by successive simulations at different growth velocities (while maintaining the same simulation box size and also the same number of nuclei per unit volume). The results for a cubic box of length $L = 5$ and and the number of nuclei per unit volume $g = 0.8$ are shown in Figure 4.

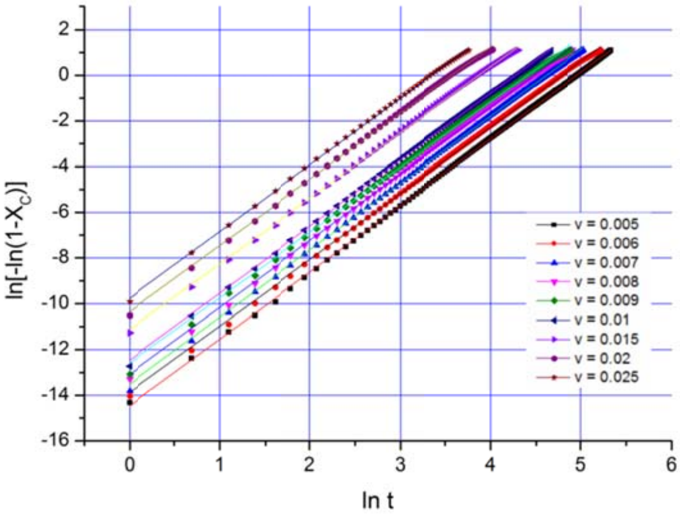

Fig. 4: Representation of the equation (6) for a cubic box with $L = 5$ and concentration of nuclei $g = 0.8$ for several growth velocities. The lines represent the individual linear fits for each set of data.

The fitted sets of data are parallel lines having the slope approximately equal with 3, as theoretically predicted for instantaneous nucleation in a 3D space [6, 7].

According with equations (4)-(6), the crystallization rate depends on the 3-rd power of the growth velocity. In order to check this behaviour, we extracted the intercepts of the linear fits from Figure 4. As resulting from equation (6), the intercept is represented by the natural logarithm of the crystallization rate. We plotted the crystallization rate as function of v^3 and we found a linear dependence (Figure 5), as it is expected for this coefficient of the Avrami equation.

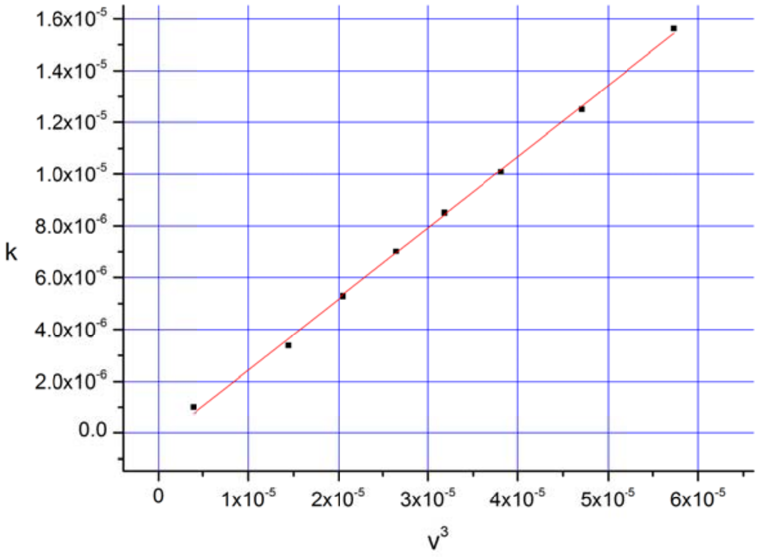

Fig. 5: Dependence of the crystallization rate as function of v^3 *for a cubic box with* $L = 5$ *and concentration of nuclei* $g = 0.8$*. The red line is the linear fit of data.*

Our simulation results were also sensitive to the starting concentration, expressed as the total number of nuclei per unit volume that were considered at the beginning of the simulation. This corresponds to the initial stage, schematically depicted in Figure 1 (a), and is expressed by the presence of g parameter in equation (4).

We systematically investigated the role of the concentration, by performing various sets of computer simulations for a cubic box with length L = 5, at a constant growth velocity v = 0.01, while considering several concentrations of nuclei.

Because the Avrami index does not depend on the concentration of the nuclei, as expected, the linear fits based on equation (6) consist in parallel lines with the same slope (having the value approximately equal with 3). These results are shown in Fig. 6.

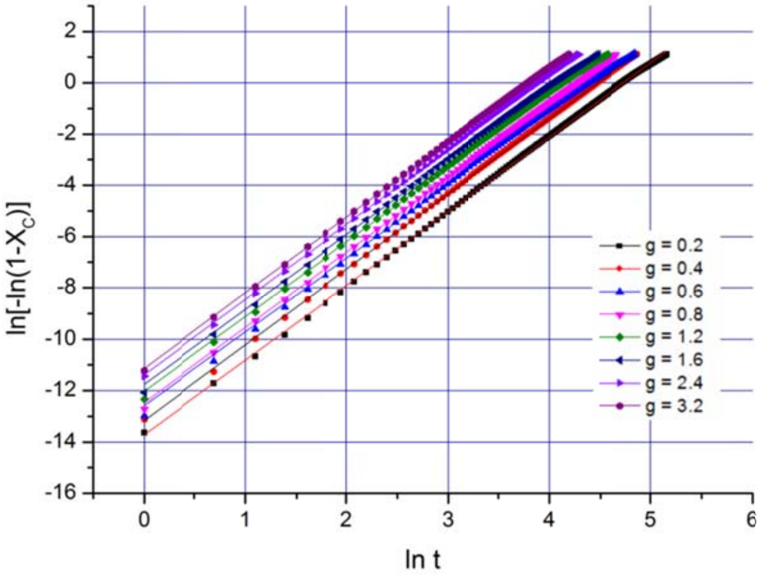

Fig. 6: Representation of the equation (6) for a cubic box with $L = 5$*, growth velocity* $v = 0.01$ *for several concentrations of the nuclei. The lines represent the linear fits for each set of data.*

Equations (4)-(6) also suggest a linear dependence of the crystallization rate constant (k) on the concentration of the nuclei (g). Using the same procedure as in the case of its dependence on the velocity, from the linear fits in Figure 6, we extracted the intercepts that provide us the crystallization rate values.

The graph of k versus concentration is presented in Figure 7 (this behaviour is also predicted by the Avrami equation).

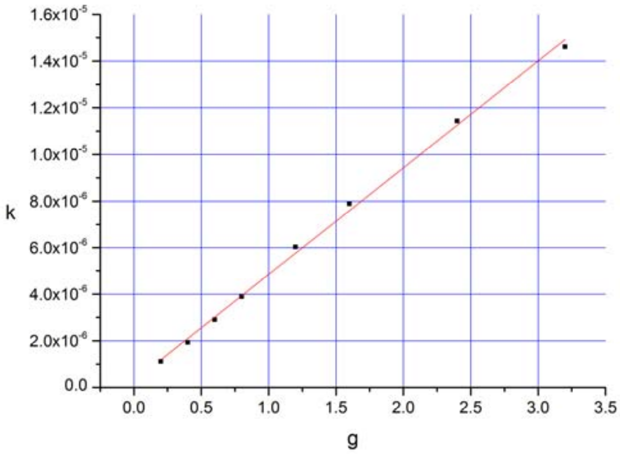

Fig. 7: Dependence of the crystallization rate as function of g for a cubic box with $L = 5$ *and growth velocity* $\mathrm{v} = 0.01$. *The red line is the linear fit of data.*

We made various simulations for the instantaneous nucleation process when considering also 2-Dimensional and 1-Dimensional systems. For the two dimensional system, we found the Avrami index $n = 2.0037 \pm 0.0008$ and the intercept $ln\,\mathrm{k} = -5.0765 \pm 0.0014$. For the one dimensional system, the results were $n = 1.043 \pm 0.007$ and the intercept $ln\,\mathrm{k} = -5.076 \pm 0.001$. These values are in excellent agreement with the theoretical predictions from [6] and [7], which state that, in the case of the instantaneous nucleation, the Avrami index is equal with the dimensionality of space. Therefore, we conclude that the Avrami model is a versatile universal tool that scientists can rely on when investigating different complex soft matter systems.

One may also notice that, for lower dimensional spaces, the results are slightly better than for the 3-Dimensional space. In our opinion, the explanation consists in the statistical fluctuations which rapidly increase as the dimensionality of the space increases.

4. Conclusions

By means of Monte Carlo simulations, we studied the transition process behavior in soft matter systems, when induced by an instantaneous nucleation mechanism. We calculated the overall crystallization rate constant and the Avrami index for various starting conditions. The results were compared with the predictions from the Avrami equation and we conclude that our computational model is in excellent agreement with the Avrami theory.

For simulations in 1, 2 and 3-Dimensional spaces, the Avrami index is equal with the dimensionality of the space, as the theoretical model predicts for instantaneous nucleation conditions. These results may also be associated to our previous work [1], where, for sporadic nucleation, the Avrami index is equal with the space dimensionality plus one (from the time parameter).

Simulations for the low dimensional spaces are to some extent better than those for higher dimensional space, result that is confirmed also for the sporadic nucleation situation [1].

The dependence of the overall crystallization rate constant (k) on the growth velocity (v) and concentration of the nuclei (g) was also examined and linked with theoretical predictions in the case of 3-Dimensional systems. Our results indicate a 3-rd power dependence on the growth velocity and a linear dependence on concentration, as also calculated from theory.

The main conclusion is that the Avrami theory is an universal tool that can be used for accurately describing phase transition processes (i.e. crystallization in soft matter systems), irrespective of the dimensionality of the space and the chosen nucleation mechanism.

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