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The kinetics of nucleation in inhomogeneous media based on the classical Avrami model

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In this paper, the kinetics of nucleation is studied in inhomogeneous media such as a mixture of the nematic liquid crystals *p*-methoxybenzylidene-*p*-butylaniline (MBBA) and *p*-ethoxybenzylidene-*p*-*n*-butylaniline (EBBA). Experimental data are analysed in terms of the classical Avrami model for nucleation. The observed non-uniform nucleation is explained within the framework of the Landau model for phase transitions. A modification to the Avrami model is proposed in order to describe the kinetics of nucleation in highly inhomogeneous media.

Key words: *Avrami model; nucleation kinetics; inhomogeneous medium; phase transformations; nematic liquid crystal; ferroelectric switching*

1. Introduction

Most of the theoretical treatments of processes occurring by nucleation and growth are based on works by Kolmogorov and Avrami [1–3]. The Avrami model was originally proposed for the process of crystal growth and describes the kinetics of nucleation on the basis of statistical considerations. This model has also been extensively applied for describing many solid-state transformations, such as crystallization from amorphous or glassy states, solidification in metallic and polymeric systems, solid-state phase transformations, adsorption and surface kinetics in electrochemical environments, and domain switching in ferroelectrics and ferromagnets. All of these phenomena take place by nucleation and growth mechanisms.

The analysis of the kinetics of these processes, based on this model, can yield physically unclear values for some fitting parameters [4, 5]. Thus, the predictions concerning the kind of nucleation kinetics based on these parameters are often inconsistent with direct microscopic observations. For example, Matyjasek showed that during the switching process in the tryglicine sulphate (TGS) ferroelectric crystal, the domain nuclei appeared almost simultaneously and in a nonuniform manner, present-

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ing so called "one-step" nucleation, contrary to the predictions based on the value of the fitting parameter suggesting a "continuous process" [6]. Such a discrepancy is clearly seen in inhomogeneous systems (i.e., ferroelectric crystals with an internal bias field [7] or nematic liquid crystal (NLC) mixtures).

In this study, we restricted ourselves to the investigation of the nucleation kinetics of thermally driven isotropic–nematic phase transition in a NLC mixture of *p*-methoxybenzylidene-*p*-butylaniline (MBBA) and *p*-ethoxybenzylidene-*p*-*n*-butyl-aniline (EBBA). In the first part, experimental data are analysed and discussed in terms of the classical Avrami model. It is shown that non-uniform nucleation can appear as a superposition of uniform ones, separated in space and time. Then, an explanation of such a superposition is given on the basis of the Landau approach to first order phase transformations. Additionally, an attempt is made to show that the Avrami model can also be applied to describe transformation kinetics in inhomogeneous media (with complex nucleation mechanisms) on the basis of more general assumptions.

2. The kinetics of nucleation within the framework of the Avrami model

The Avrami model is formulated for infinite media, i.e. the linear size of a system is much larger than the distance between the nuclei in a new phase forming during the phase transformation. The nuclei are randomly distributed over the volume of the system. Additionally, two physically different mechanisms of nucleation can be distinguished. The first, one-step nucleation, takes place when all nuclei arise only at the very beginning of the process and there is no further nucleation. The other, continuous nucleation, occurs when the nuclei continue to grow during the entire phase transformation. The growing nuclei begin to create macroscopic areas (usually called domains), which expand with a constant velocity. The rate of nucleation $R(t)$, defined as the number of nuclei per unit area and unit time, is different from zero only at the very beginning of the one-step nucleation process and is constant for continuous nucleation.

These assumptions allow a formula to be obtained for the temporal dependence of the untransformed volume fraction $q(t)$ of a system, with condition that the initial radii of all nuclei can be neglected:

$$q(t) = \exp\left(-\int_0^t R(\tau) C_d v^d \left(t-\tau\right)^d d\tau\right) \tag{1}$$

where the factor C_d is equal to 2, π or $4\pi/3$ for one, two, and three-dimensional growth of nuclei, respectively, v is the velocity of the expanding domains and d is the geometrical dimensionality of the domain growth. Thus, the transformed volume fraction $Q(t)$ of the system can be expressed as follows

$$Q(t) = 1 - \exp\left(-\int_0^t R(\tau) C_d v^d \left(t - \tau \right)^d d\tau \right) \tag{2}$$

$Q(t)$ and $q(t)$ can also be interpreted as the probabilities that an arbitrarily chosen point in the medium is respectively covered or uncovered by the growing domains.

By integrating Equation (1), with $R(\tau) = R\delta(\tau)$ for the one-step process and $R(\tau) = R$ = const for the continuous process, one can find

$$q(t) = \exp\left(-RC_d v^d t^d \right)$$

for one-step nucleation, and

$$q(t) = \exp\left(-RC_d v^d t^{d+1} \right)$$

for continuous nucleation.

Introducing a characteristic time t_0 and an effective dimensionality n (also called the Avrami exponent), Equation (2) can be rewritten for the both mechanisms of nucleation in the following form

$$Q(t) = 1 - \exp\left[-\left(\frac{t}{t_0} \right)^n \right] \tag{3}$$

The characteristic time t_0 and the effective dimensionality n are respectively equal to $1/v(1/(RC_d)^{1/d}$ and d for one-step nucleation and $((d + 1)/(RC_d v^d)^{1/(d+1)}$ and $d + 1$ for continuous nucleation. It is clearly seen that, according to the model assumptions, the Avrami exponent n should be an integer and not larger than four ($n = 4$ for three -dimensional growth, $d = 3$) and continuous nucleation ($n = d + 1$). Other values of n imply a more complicated process of nucleation, with different contributions of the one-step and continuous mechanisms.

In the case of complex nucleation ($n \notin \{1, 2, 3, 4\}$), an estimated expression for $R(t)$ can be obtained by comparing Equations (2) and (3). Thus, by using the Laplace transformation we have

$$R(t) = a(n, v, d, t_0) t^{n-d-1} \tag{4}$$

where

$$a = \left| \frac{\Gamma(n+1)}{\Gamma(n-d)\Gamma(d+1) C_d v^d t_0^n} \right|$$

The values of the Avrami exponent n, characteristic time t_0 and velocity of domain wall motion v are measured in the experiment.

Expression (4) allows information about the mechanism of nucleation and the number of nucleation events per unit area and time to be obtained.

3. Experimental

MBBA and EBBA nematic liquid crystals were mixed in the proportions 2:1. In the examined NLC mixture, the temperature of transition from the isotropic to the nematic phase was about 323 K. The transition temperatures are different for MBBA and EBBA – 319 K and 353 K, respectively. The mixture, with a thickness of 0.01 mm and a surface area of approximately 1.98 mm^2, was placed in a heater and observed under a polarizing microscope during a cooling process from 355 K through the transition point with the rate of 0.008 K/s. During the transformation from the isotropic to nematic state, the process was recorded with a video camera and the images were processed by a microcomputer. Two particularly interesting regions of the sample with a significant difference in nucleation kinetics were revealed. Experimental data were analysed in terms of the Avrami theory.

4. Experimental results and discussion

Direct observation of the isotropic–nematic phase transition in the NLC mixture revealed the existence of regions with uniform and non-uniform nucleation. Figure 1 presents a temporal evolution of the domain nuclei pattern of the nematic phase in the area with a nearly uniform initial distribution of nuclei (Fig. 1a).

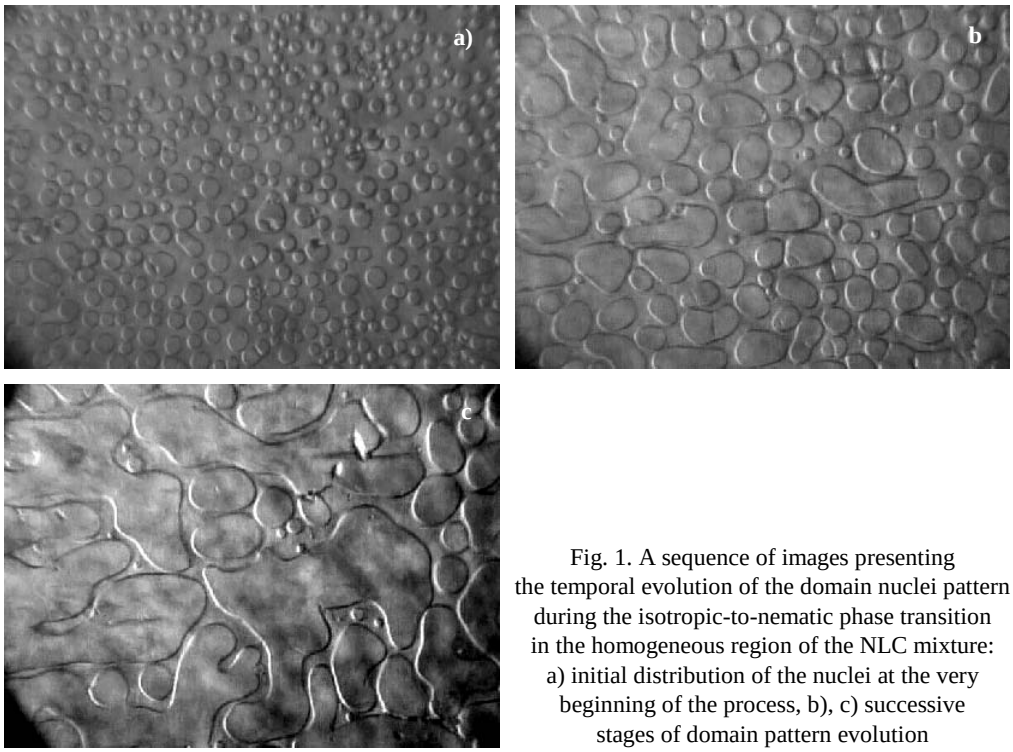

Fig. 1. A sequence of images presenting the temporal evolution of the domain nuclei pattern during the isotropic-to-nematic phase transition in the homogeneous region of the NLC mixture: a) initial distribution of the nuclei at the very beginning of the process, b), c) successive stages of domain pattern evolution

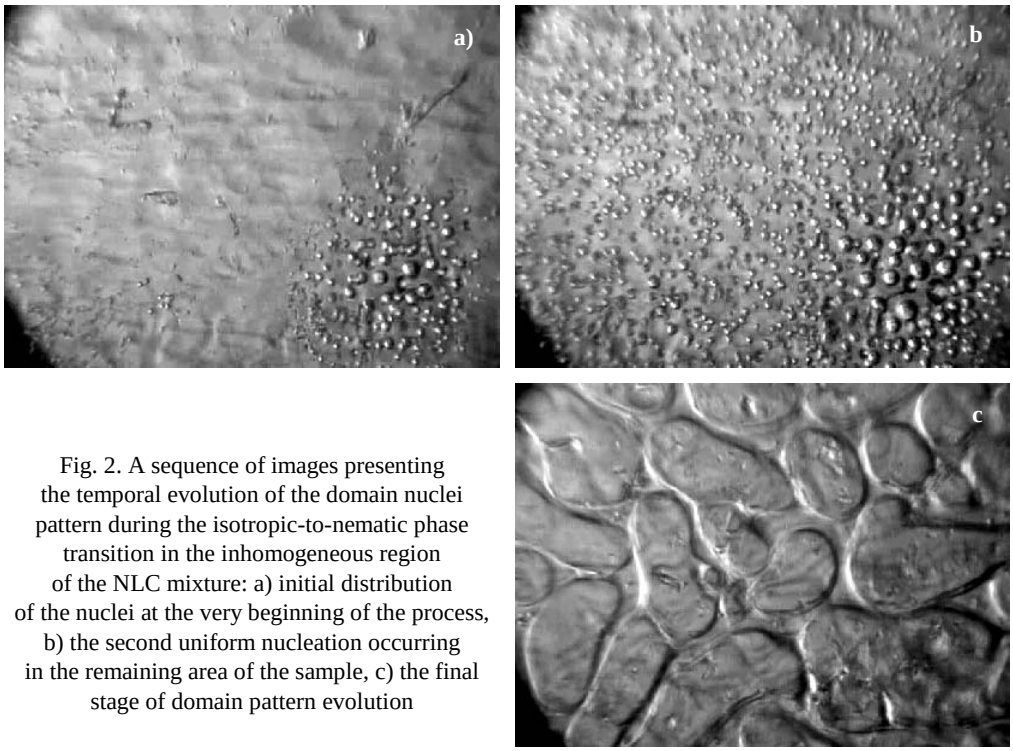

Fig. 2. A sequence of images presenting the temporal evolution of the domain nuclei pattern during the isotropic-to-nematic phase transition in the inhomogeneous region of the NLC mixture: a) initial distribution of the nuclei at the very beginning of the process, b) the second uniform nucleation occurring in the remaining area of the sample, c) the final stage of domain pattern evolution

Figure 2 shows the same process in the inhomogeneous region. From the figures, it is clearly seen that the nucleation processes are initiated with the creation of circular nuclei expanding two-dimensionally, but afterwards anisotropy appears in the expansion of some domains, and finally they begin to coalesce (Figs. 1c and 2c). It was found that the velocity of domain wall motion is constant and equal to about 0.001 $mm \cdot s^{-1}$ for the both investigated areas. The whole phase transformations took approximately the same amount of time (~115 s), regardless the kind of nucleation kinetics. Furthermore, the process of nucleation in the inhomogeneous region seems to be composed of two one-step nucleation processes, separated in time and space (compare Figs. 2a and 2b). At the beginning, the nuclei cover almost 28% of the whole surface area, then a second one-step nucleation occurs in the remaining surface area.

Figure 3 presents the temporal dependences of the fractions of the transformed phase, obtained by fitting the experimental data to Equation (3) by the least squares method. The values of the fitting parameter n are presented in the plot. The solid curve shows the results obtained for the homogeneous region, while the dotted one for the inhomogeneous region. For comparison, the dashed line shows the kinetics of nucleation only in the homogeneous part of the inhomogeneous region as seen in Figure 2a. The value of $n = 3.05$, obtained for the inhomogeneous part of the NLC sample, suggests a continuous nucleation process ($d = 2$, $n = d + 1$, see Eq. (3)) contrary to the results of the microscopic observations mentioned above. By using Equation (4), the temporal dependences of nucleation rates can be calculated. These de-

pendences, seen in Figure 4, confirm the almost one-step nucleation kinetics in the mentioned homogeneous regions.

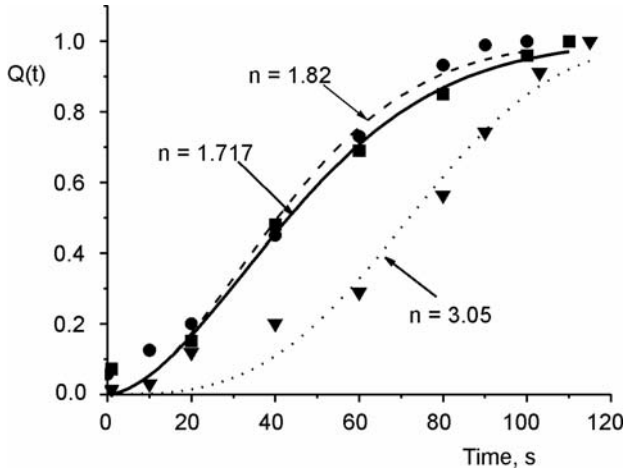

Fig. 3. Temporal dependences of the fraction of the transformed phase $Q(t)$ for three various regions of the NLC mixture: solid curve – homogeneous region (Fig. 1), dotted curve – inhomogeneous region (Fig. 2), dashed curve – small homogeneous area within the inhomogeneous region (Fig. 2a)

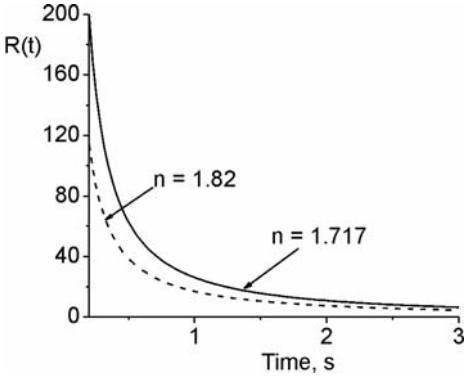

Fig. 4. Temporal dependences of the nucleation rate $R(t)$ for the homogeneous region (solid line) and small homogeneous region within the inhomogeneous one (dashed line), calculated by means of Eq. (4)

Figure 5 presents a plot of the number of all single domains as a function of time for the two investigated regions. The influence of the second one-step nucleation on the kinetics of the phase transformation in the inhomogeneous region is seen as a displacement of the maximum on the time axis. As it can be seen from the microscopic observations, the beginning of domain coalescence appears at the maximum of each curve. There is also no significant difference between these curves.

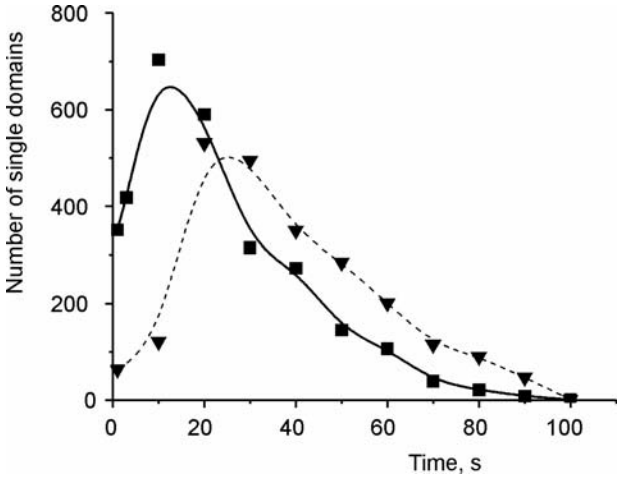

Fig. 5. Temporal dependences of the number of single domain nuclei for the homogeneous and inhomogeneous regions of the NLC mixture: solid curve – uniform nucleation, dashed curve – two one-step nucleation processes separated in time and space

From the above discussion it is clear that predictions based on the value of the Avrami exponent can yield incorrect results concerning the mechanism of nucleation.

5. Interpretation of the experimental data within the framework of the Landau model

The revealed complex character of nucleation kinetics in the inhomogeneous region of the NLC mixture can follow from a non-uniform distribution of the mixture components. This non-uniformity may strongly influence the distribution and values of the local temperatures of phase transformation and hence affect the time and type of nucleation kinetics in various regions of the medium. They may also produce the temporal and spatial separation of successive nucleation processes in various parts of the sample.

The influence of the concentration on the value of the local transition temperature can be explained in the framework of the classical Landau theory of phase transformation. Expanding the density of free energy F in powers of an order parameter p up to the third order, and assuming the coefficient of the second power of the order parameter to be temperature- and concentration–dependent, we can write

$$F = F_0 + \frac{1}{2}\left[a\left(c_c - c\right) + a'\left(T - T_c\right)\right] p^2 + \frac{1}{3}Bp^3 + \frac{1}{4}Cp^4 + \ldots \tag{5}$$

where c and c_c denote a common and a critical concentration, respectively, and $B < 0$ as appropriate for the first order phase transformation [8, 9]. From the above expansion it is clearly seen that an ordered (nematic) phase is stable for $T < T_c$ and $c > c_c$.

Otherwise, an isotropic phase exists. The natural equilibrium condition $F = 0$ leads to an inequality describing the existence of the stable phase

$$a(c_c - c) + a'(T - T_c) < \frac{2B^2}{9C} \tag{6}$$

Finally, for the transition temperature T_t we obtain

$$T_t = T_c + \frac{2B^2}{9C} - \frac{a'}{a}(c_c - c) \tag{7}$$

This formula is a phenomenological confirmation of our interpretation of the experimental data. A more detailed study of this problem in the case of first and second order phase transformations is presented in [10].

6. A generalization of the Avrami model assumptions

The description of the nucleation kinetics of first order phase transformations in inhomogeneous media on the basis of Avrami theory also seems to be possible, but in the framework of more general assumptions. In relaxor physics, an approach based on the Gaussian distribution of the local Curie temperatures around an average T_c is used to describe the diffuse phase transitions (DFT)

$$f(T, T_c, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{\left(T_c - T\right)^2}{4\sigma^2} \right] \tag{8}$$

where σ stands for the width of the Gaussian distribution [11].

Nucleation in a medium with a great number of temporally and spatially separated regions with homogeneous nucleation kinetics (one-step or continuous) is a similar problem. In such a case, the application of the Gaussian distribution of characteristic nucleation times t_{0i} around the value t_0 obtained by fitting experimental data to Eq. (3) may give correct results. This generalized assumption can be expressed as follows

$$Q(t) = \frac{\text{const}}{\sqrt{2\pi}\sigma} \int \left[1 - \exp\left(-\left(\frac{t}{t_{0i}} \right)^n \right) \right] \left[-\frac{\left(t_0 - t_{0i}\right)^2}{4\sigma^2} \right] dt_{0i} \tag{9}$$

where now $n \in \{1, 2, 3, 4\}$ and t_0 and σ are the fitting parameters.

7. Conclusions

It was found that the transition from the isotropic to nematic phase in an MBBA and EBBA NLC mixture occurs by almost one-step nucleation processes and a further growth of domain nuclei. The nucleation rates are then rapidly decreasing functions of time. It was revealed that, due to the nonuniform distribution of mixture components, the one-step processes of nucleation can be temporally and spatially separated. This separation has been explained within the framework of the classical Landau model for first order phase transformations by assuming the concentration dependence of the first coefficient in the free energy expansion. Nonuniform nucleation, observed in the inhomogeneous region, is a result of such a separation. It was shown that interpretations concerning the kinetics of nucleation performed on the basis of the Avrami exponent n may lead to incorrect results.

The application of the Avrami model for describing the kinetics of nucleation in highly inhomogeneous media (with a great number of separated areas with homogeneous nucleation kinetics), however, seems to be possible on the basis of a more general approach. Such an approach has been proposed on the basis of a model for DFT developed in relaxor physics.

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