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Yoshihisa Enomoto [a] & Shigetsugu Iwata [a]

[a] Department of Environmental Technology, Nagoya Institute of Technology, Gokiso, Nagoya, 466-8555, Japan

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Kinetics of Nematic Ordering in a Model Porous Medium

YOSHIHISA ENOMOTO and SHIGETSUGU IWATA

Department of Environmental Technology, Nagoya Institute of Technology, Gokiso, Nagoya 466–8555, Japan

Employing a time dependent Ginzburg–Landau type model for nematic liquid crystals in two dimensions, we study the kinetics of nematic ordering in a porous medium following a zero temperature quench from the isotropic phase. We consider various geometrical properties of computer generated model porous media, and compute nematic domain growth laws and scaling functions. Two–dimensional simulation results demonstrate that the growth process slows down dramatically in the presence of a surface anchoring field, which is observed in experiments. Especially, in porous media of a high porosity, we find a nonalgebraic growth of the nematic domain and also a breakdown of the dynamical scaling when the domain size becomes comparable to the average pore diameter. It might be due to the fact that an interconnected and tortuous structure of porous media creates barrier to ordering process.

Keywords: nematic ordering; porous medium; nematic glass

INTRODUCTION

Nematic ordering of liquid crystals contained within a porous medium such as Vycor glasses and silica gels has been the subject of considerable recent research [1–6], because of its rich behavior and poten-

tial applications. Various experimental results [1–3] indicate that the random preferential orientation of liquid crystals along the pore surface profoundly influences the dynamics of the isotropic to nematic phase transition (the surface anchoring effect), and fluctuations of the orientational order parameter relax at a much slower rate than in bulk liquid crystals (the nematic glass behavior). These experimental findings have stimulated a theoretical work [4] and computer simulation studies [5,6]. However, these studies have been restricted to rather simple situations, e.g., a simple parallelopiped pore [6] and a high porosity porous medium [5]. Thus, various phenomena observed in experiments are not yet fully understood.

Under these circumstances, computer simulations in a realistic model system are highly desirable for an insight into such a complex problem. In this paper, as a first step attempt, we carry out two–dimensional simulations of a model of nematic liquid crystals confined in computer generated model porous media with varying their porosity and connectivity. The novelty of this study is that the model porous medium considered here has a variety of surface structure of the pores. In Sec.2 we present the model studied in this paper, which consists of a two–dimensional spin nematic model in the presence of a porous medium. We also describe the method to construct the model porous media and the computational techniques used in the simulations. The results are presented in Sec.3. Sec.4 concludes the paper.

THE MODEL

We here study the kinetics of nematic ordering in two dimensions in a porous media, following a zero temperature quench from the isotropic phase. Considering the complexity of the problem and also a first step simulations, we adopt the following simple model for nematic liquid crystals. Nematic liquid crystals in two dimensions are described in terms of a two–components headless unit vector field (called the director field), defined on a square lattice with periodic boundary conditions. That is, we model the two–dimensional nematics by a rigid rotor Hamiltonian (called the spin nematic model

[7] or the Lebwohl–Lasher model [8])

$$H = -J \sum_{<ij>} (\mathbf{S}_i(t) \cdot \mathbf{S}_j(t))^2 \tag{1}$$

where $\mathbf{S}_i(t)$ is the director field on a two–dimensional square lattice site i at time t with a positive coupling constant J, and $\sum_{<ij>}$ denotes the summation over all pair sites of nearest neighbors. This is a simplest model that captures the physics of the liquid crystal system. In fact, the present model is identical to the standard Franck model with one constant approximation, where the moduli for splay, bend, and twist are equal [7].

The equation of motion for the director field for a zero temperature quench is given by the nonconserved time–dependent Ginzburg–Landau type equation [7] (we set $J = 1$)

$$\frac{d}{dt}\mathbf{S}_i(t) = \sum_j (\mathbf{S}_i(t) \cdot \mathbf{S}_j(t))\mathbf{S}_j(t) - \sum_j (\mathbf{S}_i(t) \cdot \mathbf{S}_j(t))^2 \mathbf{S}_i(t) \tag{2}$$

where the second term has been introduced as an effective field at site i to preserve the length of directors with the site j being nearest neighor to the site i. As required, the above model is invariant under local spin inversion, $\mathbf{S}_i(t) \rightarrow -\mathbf{S}_i(t)$, because the director of liquid crystals is a headless vector.

A model porous medium used in our simulations is constructed by using a method suggested by Chakrabarti [9]. The underlying theory to produce a computer–generated porous medium is th dynamics of a first order phase separation process in a binary mixture. The dynamics is usually described by a Cahn–Hilliard equation for the the local concentration difference, $C(\mathbf{r}, t)$, of the two components (called the order parameter), which is assumed to take continuous values anywhere from -1 to $+1$. This equation is numerically solved on a two–dimensional square lattice with periodic boundary conditions and the lattice spacing being one. From an initial zero value of the order parameter on an average with small randomness (i.e., a 50:50 mixture of the two components), as the coarsening time t_{co} (in arbitrary unit) increases the separation process drives the field variable toward either $+1$ or -1. To generate various types of porous systems, Chakrabarti has introduced a cutoff value for the order parameter, C_{th}, such that lattice sites with $C(\mathbf{r}, t) \leq C_{th}$ are regarded as the

pore space, and the sites with $C(\mathbf{r}, t) > C_{th}$ as the glass. By changing values of t_{co} and C_{th} as two tunable parameters, one can prepare model porous media of different geometrical properties. Four model porous media used here are shown in a 80×80 section of the 256×256 system in Fig.1 for different t_{co} and for different C_{th}, where the white region corresponds to the pores and black region corresponds to the glass. Table 1 summarizes the geometrical characteristics for these four porous media with volume fraction of pores (p, called the porosity), average pore diameter (d_p in the unit of the lattice spacing), and the pore surface to the system volume ratio (S/V).

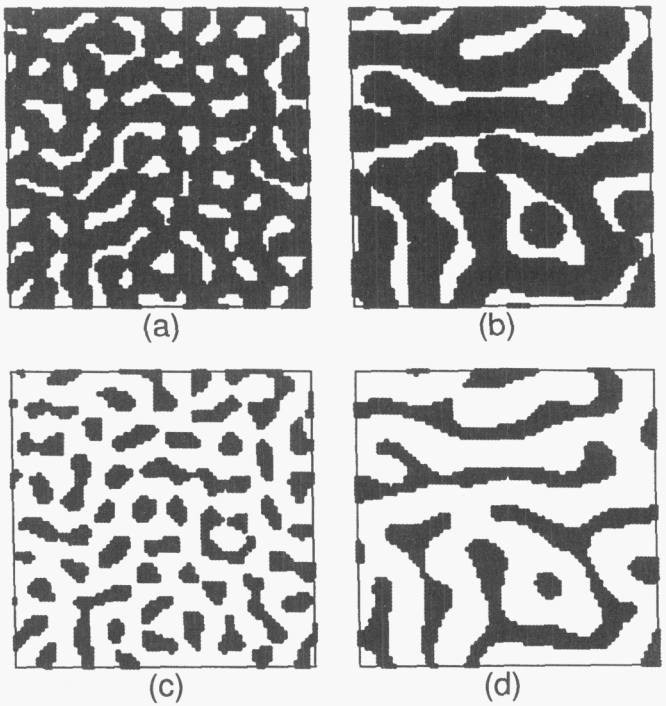

FIGURE 1 Computer genarated model porous media for (a) $(t_{co}, C_{th}) = (20, -0.337)$, (b) $(100. - 0.723)$, (c) $(20, 0.337)$, and (d) $(100, 0.726)$

sample	t_{co}	C_{th}	ϕ	d_p	S/V
case a	20	-0.337	0.3	3.4	0.23
case b	100	-0.723	0.3	4.5	0.17
case c	20	0.337	0.7	5.8	0.29
case d	100	0.726	0.7	10.3	0.19

TABLE 1 Geometric characteristics of model porous media shown in Fig.1

Once the porous medium is constructed, we solve the above equation (2) on the 256×256 porous system using a simple Euler method with a time step 0.01 up to a final time 10^3 (in proper rescaled units). As the initial condition, we set all the $\mathbf{S}_i(0)$ to have random orientations and unit length, except for $\mathbf{S}_i(t) = (0, 0)$ at the location of the glass. The boundary conditions imposed are the following: First, no flux is allowed through the impenetrable glass region. Second, the presence of a surface anchoring field on the pore surface is handled by adding a term $-\sum_i(\mathbf{h}_i \cdot \mathbf{S}_i(t))^2$ to the Hamiltonian (1), where the summation is restricted to sites on the surface [5]. In the present simulations, we consider only one kind of anchoring conditions, that is, a homeotropic anchoring with its strength $h \equiv |\mathbf{h}_i|$, where the surface anchoring field $\mathbf{h}_i$ points in a direction normal to the local tangent plane at the surface site i.

The structure formation in the system during the nematic ordering process is analyzed in terms of the time dependent structure factor [7]

$$S(\mathbf{k}, t) \equiv \sum_i < 2(\mathbf{S}_i(t) \cdot \mathbf{S}_0(t))^2 - 1 > \exp(-i\mathbf{k} \cdot \mathbf{r}_i) \qquad (3)$$

where $\mathbf{r}_i$ denotes a two–dimensional position vector of the lattice site i and the bracket $< \cdots >$ represents an average over initial configurations. Moreover, as a measure of the nematic domain size, we use the first moment of the circularly averaged structure factor $S(k, t)$ with $k = |\mathbf{k}|$, which is defined by $R_g(t) \equiv \sum_k kS(k, t)/\sum_k S(k, t)$. Assuming the dynamical scaling holds for the nematic liquid crystals, the structure factor has the scaling form [7] as $S(k, t) = R_g(t)^d g(kR_g(t))$ with the spatial dimensionality d. We study the structure formation with varying the surface field strength and also geometrical properties of porous media. In all cases, measured quantities are averaged over ten runs for different initial conditions.

SIMULATION RESULTS

Before discussing the complicated situations, we first study the nematic ordering from the isotropic phase in the bulk system with the porosity $p = 1$ and no anchoring field. In Fig.2 we show the time evolution of the director field quenched from the isotropic to nematic phases in a 80×80 section of the 256×256 system. We can see the well–known nematic ordering process [7]. The scaling behavior of the structure factor is also confirmed in Fig.3 with the growth law $R_g \sim t^{0.41}$ and the power law tail $S(k,t) \sim k^{-4.2}$, which are consistent with a previous work [7].

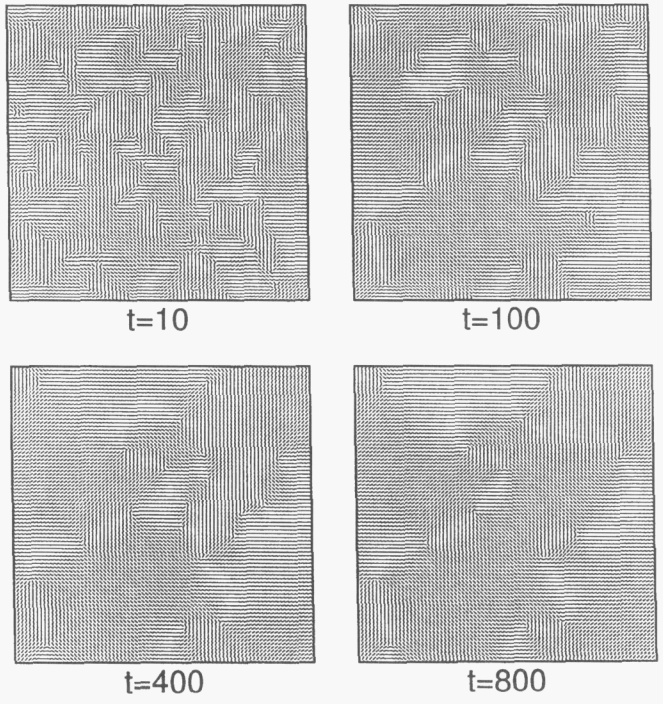

FIGURE 2 Nematic ordering process in the bulk system. Director fields are represented by lines with respective orientations and unit length.

Next we study the ordering process in low porosity media such as Vycor glasses ($p = 0.3$ in the simulation). A log–log plot of the average nematic domain size $R_g(t)$ versus t is shown in Fig.4 for the porous medium shown in Fig.1(a) (the case (a)). The similar behavior of $R_g(t)$ has been obtained for the case (b). For $h = 0$, it is found that the growth exponent is the same as in the bulk system. As was pointed out previously [6], it might be due to the vector nature of the order parameter, in comparison to a slow growth of binary mixtures in a porous medium without anchoring fields. On the other hand, as the strength of the surface field is increased, the growth law exponent is shown to cross over from a value of 0.42 to a value of about 0.22. At present, the physical origin of the exponent 0.22 at late stages is unknown. These crossover behaviors are analogous to those in a single pore model [6], although they are three–dimensional simulations. It is understood as follows: due to the small independent pores (case a) or low ration of the average pore diameter to the pore length (case b), interporous interactions can be neglected, and thus a single pore picture is valid in these low porosity media.

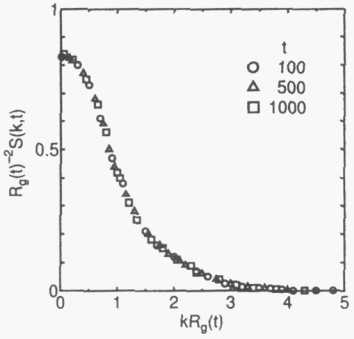

FIGURE 3 Scaling function of the structure factor in the bulk system

Finally, we study the high porosity effect, such as silica gels, on the ordering kinetics ($p = 0.7$ in the simulation). In Fig.5 we plot the average domain size $R_g(t)$ as a function of time t for the case (d). It is found that for $h > 0$ the domain growth is very slow when the average domain size becomes comparable to the average pore size

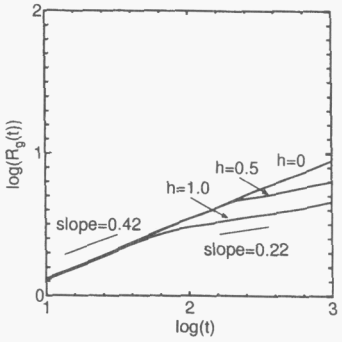

FIGURE 4 Time dependence of the average nematic domain size $R_g(t)$ for different anchoring field strength h

(almost 10 lattice spacings). Note that the data in this region are not consistent with a simple power law dependence as $R_g \sim t^n$. We have also tried to fit R_g to several function forms such as $\log(t)/t^m$, but again without success. Such a nonalgebraic growth law suggests that there is more than one length scales in the problem. This might lead to a breakdown of the dynamical scaling behavior, as was expected in a binary liquid mixture contained inside a model porous medium [9], which resembles the present medium. We have tested the scaling hypothesis for the structure factor for the case (d) with $h = 1$, as shown in Fig.6. It is clear from this figure that the data are quite scattered. Thus, the scaling hypothesis seems to break down during the growth process. The similar behavior has been obtained for $h = 0.5$ as well as the case (c). Snapshots for the liquid crystal conformations help us understand the situation. In Fig.7 we show the time evolution of the director field in a 80×80 section of the full system for the case (d) with $h = 1$. From these figures it is found that due to an interconnected and tortuous structure of pores separated by pore junctions the system firstly break up into many nematic domains (subsystem) where the ordering occurs independently in each subsystem, and after their average size is comparable to the pore diameter, such independently ordering subsystems hardly grow further. That is, it seems that the interconnected tortuous structures of the confining geometry (an interporous interaction) might play an important role in the nematic ordering process by collectively cre-

ating extra barriers to domain growth [9], in contrast with the low porosity media where such a interaction can be neglected. This feature is similar to the nematic glass behavior observed in experiments [1–3]. To discuss the relationship between the breakdown of the scaling hypothesis and the nematic glass, we need study the relaxation of autocorrelation function of the orientational order parameter. This is beyond the scope of the present work and is now under the way.

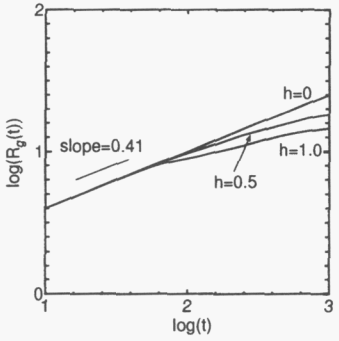

FIGURE 5 Time dependence of the average nematic domain size $R_g(t)$ for different anchoring field strength h in a porous medium shown in Fig.1 (d)

CONCLUSION

In summary, we have carried out two–dimensional simulations of the spin nematic model to study the nematic ordering kinetics confined in computer–generated model porous media following a zero temperature quench from the isotropic phase. We have studied effects of surface anchoring fields and porous geometries, and computed the domain growth laws and the scaling functions.

We have summarized main results: (1) In the absence of any anchoring field the growth law exponent of nematic domains is the same as in the bulk system. In comparison to a slow growth in binary liquid mixtures in porous media, it is thought to be due to the vector nature of the order parameter of liquid crystals; (2) In low

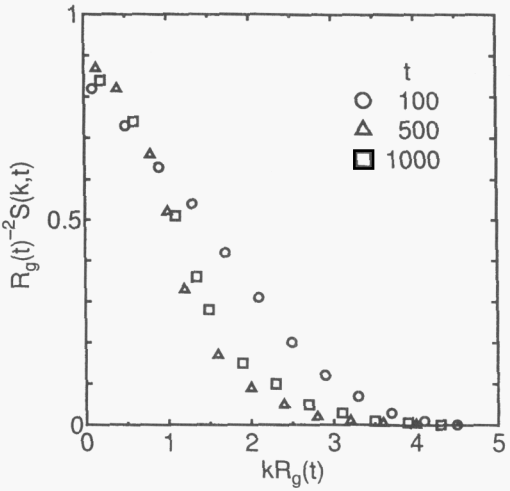

FIGURE 6 Breakdown of the scaling behavior for the structure factor in a porous medium shown in Fig.1 (d) for $h = 1$

porosity porous media such as Vycor glasses the growth law exponent crosses over from 0.42 (the bulk value) to 0.22 as the anchoring field is increased; (3) In high porosity porous media the growth of nematic domains is slow as the average domain size becomes comparable to the average pore diameter, and the dynamical scaling breaks down as well. It seems that the geometrically induced interporous interaction creates barrier to further growth and leaves the system with many different length scales.

Unfortunately, it is difficult to relate our results to experimental observation directly, due to the combination of defects such as the low dimensionality, the short–range nature of the surface anchoring field, zero temperature quench, and so on. However, the present model has been found to be potentially rich and exhibit fascinating phenomena to be useful for an insight into the complex problem. Thus, it would be interesting to perform more realistic simulations by considering effects of three dimensionality, long–range anchoring conditions and thermal fluctuations, as well as discussion on transport properties, relaxation of the orientational order parameter, and effects of other types of porous structures. These are now under the way.

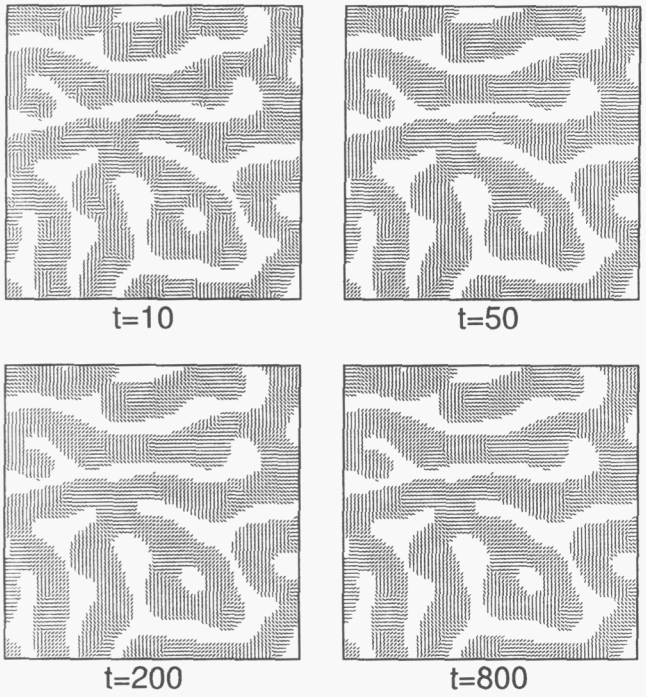

FIGURE 7 Nematic ordering process in a porous medium shown in Fig.1 (d) for $h = 1$. Director fields are represented by lines with respective orientations and unit length.

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