KINETICS OF TEMPERATURE OR PRESSURE FIELD INDUCED PHASE TRANSFORMATION IN LIPID BILAYERS*

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A description of kinetics of the temperature or pressure field induced phase transformations in model biomembranes is proposed. It is based on the Avrami-Kolmogorov model combined with concept of chemical reaction fractal-like kinetics. As a result, a non-Debyean (stretched exponential and power-law) relaxation of the phase transformation process is obtained. Possible applications to experimental cases like thermotropic phase transformations in lipids (*e.g.* dipalmitoyphosphatidylcholine - DPPC) and/or hydration of dioleylphosphatidylethanolamine (DOPE) bilayers caused by pressure are discussed.

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1. Introduction

Amphiphilic assemblies, such as lipids and surfactants dispersed in water or other (*e.g.* organic) solvents can undergo aggregation into a variety of physico-chemical structures among which biomembranes encompass some commonly known morphological systems. They may also transform from one structural form, like gel to another like liquid crystal, when solution

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conditions are changed *e.g.* the pH-characteristics, the electrolyte concentration or some thermodynamic factors, *e.g.* temperature or pressure. Such systems may exhibit a very rich structural behavior regarding the liquid crystalline (or noncrystalline) phases with many topological arrangements of components from which they are constituted. Under certain physicochemical circumstances, generally due to a cooperative behavior of a lipid solution, biomembranes are observed to form regular (periodic) lattices in one- , two- or even three-dimensional spaces [1]. The resulting structures usually resemble the smectic liquid crystals because of existence of stacks of amphiphilic layers, mostly separated by water. Some lamellar as well as nonlamellar (like inverted hexagonal or cubic) phases, or even the intermediates called mesophases, can also emerge which is of relevance when investigating some biological processes like domain or cluster growth, channel formation within a biomembrane, phase separation, fusion, thin film rupture, *etc.* [2]. There is also a possibility of forming some more irregular statistically self-similar ensambles (sponge-like or reminiscent of the percolation lattice) when some defects or structural perturbations, like anaesthetics, impurities, some interstitially located molecules or thermal as well as athermal (*e.g.* due to domain surface) fluctuations of the membrane material, are detected in the system [3]. This is certainly a case which seems more realistic and would be more likely to occur in real biosystems in which biomembranes represent the main structural constituent for their pretty complex architecture [4].

This is now rather commonly accepted opinion that dynamics of a thin model biomaterial examplified by the lipid bilayer and manifested by phase transformations caused by change of an external field (*e.g.* temperature or pressure), is one of the most attractive and not completely solved problems. In order to understand kinetic aspects of the phenomena mentioned above, one requires not only a proper understanding of the thermodynamics of self-association in the lipid dispersions, but also of temporal rules driving the process, *i.e.* how the new phase may arise from the old one. An important problem is usually related to a general feature of how the interaction forces between amphiphiles within aggregates are affected by certain solution conditions, like pH or temperature, *etc.*, and how to incorporate it into a rather phenomenological kinetic description [5, 6].

In this study, we propose a novel approach for description of the kinetics of thermo-(*i.e.*, caused by temperature changes) as well as barotropic (*i.e.*, pressure mediated changes) phase transformations in model biomembranes. For illustration, we have chosen two kinds of examples that, in our opinion, could be described in the frame of our modeling. First, we make an attempt in order to elucidate relaxation kinetics obtained *e.g.* during the dilatometric experiments on quenched dipalmitoylphosphatidylcholine (DPPC) systems where the classical kinetic effects but with small fractional dimensionalities

may occur [6] or when measuring hexagonal/cubic and cubic/lamellar phase transformations in a lyotropic liquid crystal [7]. Second, we consider another related phenomenon, in which some action of the hydrostatic pressure imposed on a hydrated dioleylphosphatidylethanolamine (DOPE) membrane sample plays a predominant role. Let us describe this case in more detail because it looks very interestingly. So, following [8], one has to report that the DOPE model membrane, comprised of inverted hexagonal phase, is prepared by mechanical mixing to be fully hydrated. It results in a more or less homogeneous swelling of the membrane material. In consequence, the macromolecules constituting the bilayer get elongated since the water molecules enter the whole porous membrane structure. The entrance proceeds rather througout the pre-existing pores or some free volume spaces located among lipid macromolecules than by transient fluctuations of the bilayer structure. Some additional but equally important effects relying on the electrostatic attraction between the water molecules (or some aggregates of them) and the lipid chains is to be noticed as well. What does really happen after exerting the hydrostatic pressure of order of 1 kbar on the swollen and hydrated DOPE membrane system? From the physico-chemical point of view, one realizes that the chemical potential of the bulk water present in the system is changed which results in some migration (diffusion) of the molecules throughout the spatially fluctuating membrane material; note that these fluctuations can be mostly thought of as a direct response of the membrane material on the pressure action. Some resulting spatial reorganization of the water molecules and/or water complexes emerges, and a certain possibly electrostatic association of water to lipid macromolecules or domains establishes the hydration process and provides its quite firm coupling to the lipid structural changes in which, in our opinion, none of the processes prevails or dominates. The last sentence is, however, our hypothesis. It may come from the following rationale. Namely, if the lipid structural changes were slow compared to hydration then hydration kinetics will perfectly follow those of the lipid, in other words, the hydration can be monitored. If hydration were slow, in turn, then the rate limiting step would be that of hydration of the new structure. The former must be discarded because it is not observed in the experiment [8] and simply looks unrealistically in the light of experimental conditions applied. The latter will, at most, be a specific case treated by the theory featured by this paper since it should follow first order kinetics [9], but with the chemical reaction rate coefficient being time-independent (as it will be seen further, we will describe time-dependent kinetics). Thus, we opt for the scenario in which the process is complex and consists of two unseparable parts, namely that of hydration and that assigned to the lipid structural changes. Such a process is hard to treat by simple tools. The only fruitful as well as simple way that we can see relies on presumption

that the process under study is the anomalous random walk process. It may be reminiscent of the random walk process on a percolation lattice, and can be roughly sketched as a propagation of the hydration front or "wave" (inevitably connected with the lipid structural changes) in the bilayer. Such a phenomenon may belong, in general, to the class of transport processes in a possibly fractal (not through a fractal!) matrix, where the fractality of the space may, if needed, be constructed by using *e.g.* the interfaces between lipid domains or by realizing the porosity of the structure in question. In this way, we may have some microscopic insight into the whole process mentioned. As to the phase transformation in the system, one can consider the following. Namely, after the pressure is being applied, a certain release of water molecules is noticed, the swelling conditions are changed, the hydration process is still contributed, but the system leaves the old (elongated or stretched) structural state (see above) and arrives at a new (squeezed or compressed) one. Both physical states, *i.e.* the parent and the children phases, remain hydrated. So, the phase transformation that we propose to consider is of purely mechanical nature and relies on a passage between two mechanically distinguishable states of the piece of material in question, *i.e.* between the elongated and the squeezed one. A similar picturesque explanation can also be served when an infrared milisecond laser temperature jump influences a lyotropic liquid crystal (*e.g.* non-ionic surfactant plus water) behavior. In such a case, one can study some phase transformations between mesophases formed by a non-ionic surfactant in water, like hexagonal/cubic or cubic/lamellar phase transformations [7]. Here, however, the role of hydrostatic pressure plays the laser T-jump.

Bearing that in mind, we wish to propose a modification of the Avrami-Kolmogorov (AK) equation [6, 10] due to incorporation of the fracal-like chemical reaction kinetics [11] which would be responsible for a proper description of the coupling of the hydration with the lipid structural changes, and taking into account existence of the phase transformations between two mechanically different states of the membrane constituents, like lipid macromolecules or some clusters of them. As a result, we get the temporal (kinetic) behavior of the system in question which, depending upon the range of action of a main physical parameter of the system, denoted by h, is either a stretched exponential (*i.e.*, the non-Debyean relaxation effects take place, like in case of many thermotropic phase transformations studied [6, 7]) or a power function of time (*c.f.* [8] and references therein), or may also be constant, *i.e.* a static "frozen" structure is possible to obtain.

The paper is organized as follows. In Section 2, we shortly sketch the model which can describe the pressure induced hydration kinetics in lipid bilayers and also may serve for description of other (thermotropic) phase transformations [6, 7] (our rationale is that sudden changes of the pressure

or temperature field may cause, in the frame of our phenomenological description applied, at least qualitatively the same changes in the hydrated lipid matrix). Next, we modify this model in order to adapt it for a description of anomalous kinetic behavior of the 'wet and dynamic matter system' [7, 8, 12]. The analysis of the model is carried out in Section 3. The Section 4 offers closing remarks.

2. Generalization of the Avrami–Kolmogorov equation

The Avrami-Kolmogorov (AK) kinetic theory of the temporal behavior of biphasic systems is a well-established theory and can be found elsewhere [6, 13]. One may also consult the original papers [10]. This theory describes kinetics of a physical process as to how to get temporal rules of yielding a new phase of a system at the cost of the old phase assuming that a *constant* number of nuclei constituting a system as well as a growth law for an individual nucleus are determined. Let us start directly from the generalized equation of AK-type which reads

$$\frac{d}{dt}f_h(t) = Nk(t)[1 - f_h(t)]\frac{dV_n(t)}{dt}, \tag{1}$$

where $f_h(t)$ is a time-dependent fractional completion or volume fraction of a sample transformed to a new phase [10, 13], N is a number of randomly distributed nuclei per unit volume each of which will grow to a volume $V_n(t)$ at time t. Let us notice that a stationary state, $df_h(t)/dt = 0$, is reached for $f_h(t) = 1$ (in practice, after some large time interval being passed). Keep in mind that, by construction, $f_h(t)$ always takes on the values from the interval $[0, 1]$ and is dimensionless.

Two factors in the aforepresented equation are novel when comparing to the classical description. The first is related to the quantity $k(t)$ termed in this study as the chemical reaction rate coefficient which is assumed to be a power function of time of the form [11]

$$k(t) = k_0\left(1 + \frac{t}{\tau}\right)^{-h}, \quad h \geq 0, \tag{2}$$

where k_0 is the "equilibrium" chemical reaction rate constant which depends upon temperature and τ stands for a characteristic time scale of the reactions. Let us note that for $h = 0$ one gets $k(t) = k_0 > 0$ and for long times $k(t)$ tends to zero for any $h > 0$. Profitting by the modern chemical reaction

kinetics theory [11, 14], one can state that the h-exponent might be related to the spectral dimension of the fractal or nonfractal system which, in turn, can be inferred from the probability of the system return to its initial state which is a power function of time [11]. The theory [11] offers evaluation of this exponent utilizing the Alexander-Orbach conjecture, *i.e.* $h = 1 - d_s/2$ and $d_s = 2d_f/d_w$, where d_f is the fractal dimension of the object (membrane) under study and d_w is the fractal dimension of the random walk in a biopolymeric fractal system [11, 15, 16]. On the other hand, the quantity h reflects transport properties of the system and exhibits a "connectivity" of the system, *i.e.* how likely a random walker can travel through the whole structure, how many dangling ends or traps, or steric hindrances or even interfaces the structure owns or, equivalently but in the language of chemical kinetics, how easily can the chemical reaction proceed, *etc.* [17]. In turn, for having known more details concerning the transport processes in biomembranes, mostly in the spirit of correlated (non-Markovian, "with memory") and non-correlated (Markovian, "memoryless") random walk concepts, Ref. [18] can probably shed more light on the problem studied.

The physical motivation of incorporating $k(t)$ into Eq. (1) may come from the following general reasoning. Namely, in biosystems like DOPE or DPPC membranes, the cooperative structural changes in lipid bilayers can be assigned to either the growth of lipid domains or to some kind of disruption or 'degradation' (lysis, phase separation, rupture [19], structural changes in some protein involved biomembranes caused by a ligand association or dissociation [20], defects 'provoked' by small and mobile proteins like mellitin [21], *etc.*) of the membrane material (or a part of it) caused by certain species like proteins, anaesthetics, impurities or induced by some external fields like temperature or presssure, or sometimes by some gradients (changes) of them [3, 22]. Such phenomena are related to the strength of interactions in the system that are in general the lipid-protein (or lipid-solvent) interactions [3]. If the biological process involves diffusion of some agents like water molecules within the lipid matrix and the process of water penetration proceeds in one lipid domain in a quite different time regime than in another one (*e.g.* because of trapping, caging, presence of compartmentalized reactions or building of π bonds, some disconnections of lipid domains, possible phase separations, *etc.*) then the size of the domain, its microscopic structure as well as life-time, *etc.*, must be for sure a very important physical factor. It can lead to the fractal-like reaction kinetics of the process and cannot, even crudely, be understood, because of enormous complexity, in any classical reaction-kinetic terms [11].

To be more specific, let us recall *e.g.* the gel-to-liquid crystalline phase transformation of some multilamellar lipid bilayers [13] or the pressure induced hydration of lipid model membranes. They both may be understood

by invoking the following picturesque explanation. Thus, we start from the experimental situation in which under a certain external field (temperature or pressure) something is going to happen. *E.g.* in the latter, water molecules enter the bilayer [8] and invasion of water molecules into such an elastic porous medium (*e.g.* DOPE-dispersion) proceeds. The water penetration and possible chemical reactions between water and lipid molecules lead to creation of a new swollen and hydrated phase. After the temperature or pressure action, some squeezing effects of lipid macromolecules or even of domains composed of the macromolecules are possible to observe [8] under such physical circumstances because some external cause (temperature or presssure) is exerted on the system and the water molecules or water complexes push on the lipid matrix constituents. As reported in [8, 11], the kinetics of yielding the new (squeezed) phase from the old (unsqueezed or elongated) one, is time-sensitive [8] and therefore the concept of fractal-like chemical reaction kinetics, represented by Eq. (2), is used in the paper (see also another similar elucidation concerning a defect process in a lipid bilayer described in [14]). Note that by assuming the above we have still an equation of the AK-form, but now with a time-dependent number of "nuclei" (seeds or germs) which is equal to $N(t) = N(1+t/\tau)^{-h}$ and it is a decreasing function of time, like *e.g.* in the normal grain growth of (bio)materials (see discussion in [14]). In other words, as a consequence of the assumption (2), we propose to rewrite the classical AK-equation for some number of "nuclei" $N(t)$ being time-dependent (in the classical description, it is a positive constant).

The second factor, the volume $V_n(t)$, possesses a clear and unique meaning in the AK-description. It is of the form [13, 11]

$$V_n(t) = gu^p R^3(t), \tag{3}$$

where $R(t)$ is the radius of a single possibly round domain taken at time t, g is a geometrical "shape" factor, *e.g.* for spheres it is equal to $4\pi/3$, and u is a radial growth rate (known in some typical cases like growth of sphere-like or other symmetric objects). The exponent p takes on the values which one is able to infer from the $R(t)$ versus t dependence.

Let us concentrate on the time-dependence of $R(t)$ which certainly is needed to determine $V_n(t)$ (see Eq. (3), stated above). In a general case, it has the form [23]

$$R(t) = at^{\gamma}. \tag{4}$$

For a squeezed state of the lipid chain (or domain), one has [23]

$$\gamma = 1/3, \quad a = a_0(-B/C)^{-1/3}, \tag{5}$$

where a_0 is a positive proportionality constant, and the quantities B and C are the second and third virial coefficients which enter the power expansion of pressure of the macromolecular (lipid) system around N; see [23], pp. 90-92, for having more details.

For a stretched (elongated) lipid chain state one may write [23]

$$\gamma = 3/5, \quad a = a_1 b T^{1/5}(v/b^3)^{1/5}, \tag{6}$$

where a_1 is a positive proportionality constant, T stands for the so-called reduced temperature of the system, b is the length of the monomeric unit of the lipid chain, and v stands for its excluded volume [23].

For an ideal Gaussian chain near the Flory (or θ)-temperature we can obtain [23]

$$\gamma = 1/2, \quad a = a_2 b, \tag{7}$$

where a_2 is a positive proportionality constant as well. This case is rather an intermediate ('idealistic') case and will be consequently omitted.

Notice once again that now we formulate our problem in a language of time variable (in a time domain). There exists a mathematically and also physically equivalent formulation of the problem but in terms of some variable n (instead of t) which is always referred to as a number of repeating subunites (monomers) constituting a polymeric chain (*c.f.* [23, 24] and references therein).

The above presented scaling formulas are classical in the polymer physics and hold for polymer chains which are either compressed (shortened or squezzed) by an external field as *e.g.* by pressure, or for the random polymer chain with some excluded volume effect, for which one expects to have $R(t) \propto t^{3/5}$, or for a purely random chain (with no excluded volume effect), for which one gets $R(t) \propto t^{1/2}$(*c.f.* [24] and references therein). Notice that if the squeezed structural state dominates the process in question then one expects to have to do with some non-lamellar (like inverted hexagonal [8]) phase, whereas in the case of elongated structural state some lamellar (gel or crystalline [7]) phase may prevail.

Applying Eqs. (3) and (4) one gets

$$V_n(t) = g u^p a^3 t^{3\gamma}, \tag{8}$$

which means that $V_n(t)$ increases with t.

Let us mention that Eq. (1) is reminiscent of a typical chemical reaction kinetic equation of the first order with respect to f_h (*c.f.* [11, 9] and refs. therein). Also, the f_h-variable is of the form of $f_h = V_h/V$, where V_h represents a volume of the swollen ('affected') phase and V is the total volume of the system in question and f_h simply reminiscent of the mole concentration of reacting species or their molar ratio. Moreover, let us recall once again that one should be aware that we have applied a scaling formula, *i.e.* Eqs. (3) and (4), which, among others (see above), holds for a macromolecule of radius R being squeezed by the water molecules being forced by an external (temperature or pressure) field [23].

3. Solution of the generalized Avrami-Kolmogorov equation

The proposed model is determined by Eqs. (1), (2) and (8). It is convenient to present a solution of this model in terms of a rescaled relaxation function $x(t)$ defined as [8]

$$x(t) = \frac{1 - f_h(t)}{1 - f_h(0)}, \tag{9}$$

which changes from 1 for the initial state $t = 0$ to $x_{\rm st} \in [0, 1]$ for the final state as $t \to \infty$. The solution of Eq. (1) with the functions (2) and (8) reads

$$\begin{aligned} x(t) &= \exp\left[- 3A\gamma\tau^h \int_0^t s^{3\gamma-1} (\tau + s)^{-h} ds \right] \\ &= \exp\left[- At^{3\gamma} F(h, 3\gamma; 3\gamma + 1; -t/\tau) \right], \end{aligned} \tag{10}$$

where $F(a, b; c; z) = {}_2F_1(a, b; c; z)$ stands for the hypergeometric (Kummer) function [25] and

$$A = Nk_0 g u^p a^3. \tag{11}$$

Details of dynamics of the phase transformation determined by Eq. (10) depend on h and γ. The formula (10) is rather complicated bacause of the appearance of the hypergeometric function $F(a, b; c; z)$. In Ref. [25] the reader can find many special forms of this function for specific values of the parameters a, b and c.

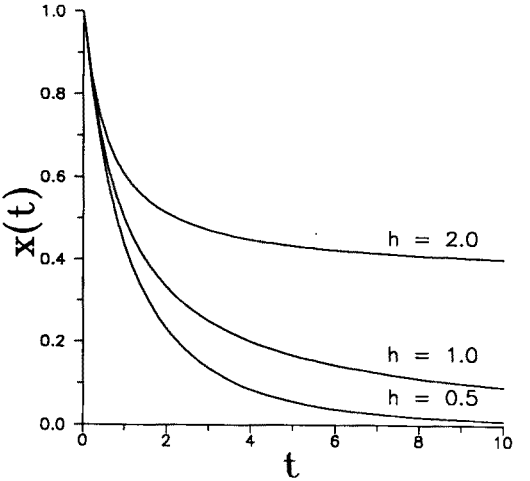

Fig. 1. The solutions (10) for the squeezed state ($\gamma = 1/3$) for different values of h: 0.5, 1.0, 2.0, respectively.

For the squeezed state, *i.e.* when $\gamma = 1/3$ (*c.f.* Eq. (5)), Eq. (10) can be expressed by elementary functions and the relaxation function $x(t)$ takes the form (*c.f.* Fig.1)

$$x(t) = \exp\left\{ -\frac{A\tau}{1-h}\left[(1+t/\tau)^{1-h} - 1\right]\right\}, \quad \text{for } h \neq 1\,, \tag{12}$$

$$x(t) = \left(1+\frac{t}{\tau}\right)^{-A\tau}, \quad \text{for } h = 1\,. \tag{13}$$

In a general case, for arbitrary values of parameters h and γ, the long-time asymptotics can be directly evaluated from (10) providing the result

$$x(t) \sim \exp[-Ct^{3\gamma-h}], \quad C = 3A\gamma\tau^h/(3\gamma - h)\,, \quad \text{for} \quad h \neq 3\gamma\,, \tag{14}$$

and

$$x(t) \sim t^{-\beta}\,, \qquad \beta = 3A\gamma\tau^{3\gamma}\,, \qquad \text{for} \quad h = 3\gamma\,. \tag{15}$$

The exact expressions (12) and (13) reduce to the form (14) and (15), respectively, for times $t >> \tau$.

Now, one can discuss all classes of solutions to the problem in question. Namely, in dependence of values of the exponent h, one can distinguish three classes of the long-time asymptotics (Figs.1-3). For the first class, when $h < 3\gamma$, the relaxation function $x(t) \to 0$ as $t \to \infty$. It is governed by the *stretched exponential*. For the second class, when $h = 3\gamma$, the function $x(t)$ decreases to zero as well but now the kinetics of the transformation process changes according to a *power-law* (15) with the exponent $3A\gamma\tau^{3\gamma}$.

For the third class, when $h > 3\gamma$, the solution $x(t)$ *approaches a positive constant value* $x_{\rm st}$. *E.g.*, if $h = 3\gamma + 1$ then $F(h, 3\gamma; h; z) = (1 - z)^{-3\gamma}$ and now one gets the exact result

$$x(t) = \exp\left[- A\left(\frac{\tau t}{\tau + t}\right)^{3\gamma} \right]. \tag{16}$$

Indeed, in the long-time limit it behaves as (14) and tends to the constant value $x_{\rm st}$ given by

$$x_{\rm st} = \exp\left(- A\tau^{3\gamma}\right) > 0\,. \tag{17}$$

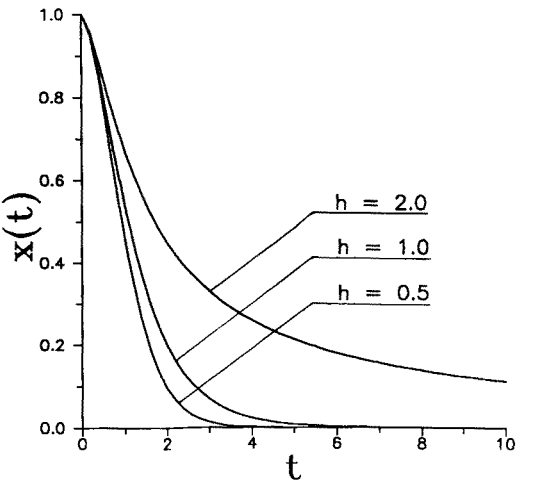

Fig. 2. Same as in Fig. 1, but for the elongated state ($\gamma = 3/5$).

It is worth stressing that the stationary solution $x_{\rm st} = 0$ corresponds to the situation when the new phase dominates the whole system and the old phase is completely pushed out by the new one. Such kind of the transformation can be examplified by either the fluid-to-ripple phase transition or the ripple-to-gel phase transition, or even the gel-to-liquid crystalline phase (cubic, hexagonal) transiton [6, 8, 12, 22]. On the contrary, if in the stationary state $x_{\rm st} > 0$ then the residue of the old phase co-exists with the new one. This situation can appear in all the biophysical systems which show a tendency to self-defence against creation of a new phase. For example, one can invoke here some immunological scenarios which typically rely on competition between two kinds of phases: the non-affected (healthy or immune) and the affected (sick or toxicated) one. If $x_{\rm st} = 0$ then all cells of the domain are affected. If $x_{\rm st} > 0$ then only a part of cells is finally affected.

The cases (12) for $h = 0$ and (14) for $3\gamma = h + 1$ correspond to the classical Debye relaxation function of the exponential form. Otherwise, (12) and (14) are always stretched exponentials with the critical exponent $3\gamma - h$ ($\gamma = 1/3$ for the case of (12)) and are known as the Kohlrausch-Williams-Watts relaxation functions being a very useful tool serving for description of the relaxation (time-dependent) phenomena in strongly interacting (non-Debyean) glassy materials and fragile liquids (*c.f.* [26] and references therein). Eq. (13) can be utilized in a specific situation studied in [8]. As the main result, the authors of [8] offer a power law for a rescaled relaxation function $x(t)$, which is deduced from the measurements of the time dependence of the number of water molecules per a lipid molecule. It is of the power law form (13), where $A\tau$ ranges from ca. 0.66 to 0.99 (see [8] for details). Therefore, it seems to us that such modeling may be promissing (*c.f.* Eq. (11)), though in some specific cases a possibly well-estimated values of $A\tau$ should be justified (unfortunately, we have no experimental findings for A and τ). For the thermotropic phase transformation (6), in turn, when $\gamma = 3/5$, a physical picture that we get is of the same quality as in the barotropic case (Fig.3). The only difference is that the kind of relaxation occur for the following values of h: if $h < 9/5$ then we get the stretched exponential behavior, for $h = 9/5$ a power-law is realized and finally for $h > 9/5$ the system reaches a positive constant value.

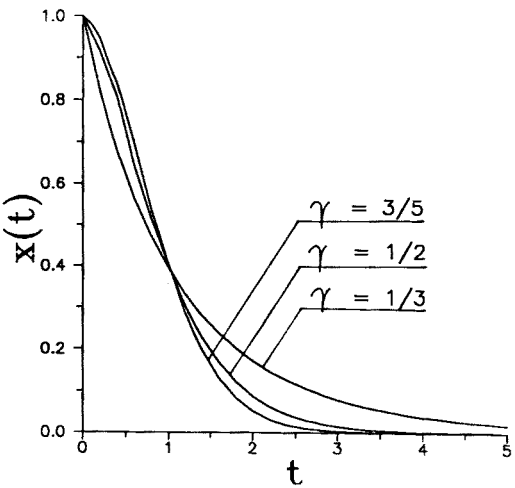

Fig. 3. A comparison of solutions (10) to the problem studied for $h = 0.2$, but for different values of γ: $1/3, 1/2, 3/5$, respectively. This represents the phase transformation from the old fully hydrated and elongated ($\gamma = 3/5$) via the normal (intermediate) hydrated ($\gamma = 1/2$) to the new hydrated and squezzed ($\gamma = 1/3$) state.

4. Closing remarks

In Section 2 we have proposed a description of the thermotropic as well as barotropic phase transformations in the frame of the modified AK-theory [10] combined with the fractal chemical reaction kinetics concept [11]. In Section 3 we have revealed some results of that modeling, mostly by stating explicitely and applying the rescaled relaxation function $x(t)$ of the system studied.

The main results of the paper are as follows:

— for the thermotropic phase transformations one is able to recover the forms of the relaxation functions reported in the literature, *e.g.* in [6, 7, 12, 13];

— for the power-law kinetics, a physical structure of the critical exponent $A\tau$ is found;

— some trends of both, theory and experimental measurements reported in [6, 13, 7] as well as in [8] and represented by the rescaled relaxation function $x(t)$ (see the equations presented in the previous section), are in a good agreement, though an exact fitting to the experimental data from [8] is not provided;

— the description reconstructs the physical picture of the situation modelled which consists of: phase transformation between the elongated (or stretched) and squeezed (or compressed) states of the system which is implicitly associated with the microdomain growth and structure formation, like in [14, 27], or even broader, *i.e.* like in the nucleation-and-growth mechanism [7], and fractal-like reaction concept which couples the hydration and lipid structural changes of the membrane material (these phenomena are accompanied by a rather homogeneous swelling of the system [7, 8, 12]); note formally that the situation described is not necessarily restricted to deterministic or random fractals, but can also be assigned to some typical Euclidean objects like spheres or cylinders (in biophysics: micelles or vesicles) or even flat sheets (*viz.* phospholipid monolayers or bilayers dispersed at the air-water interface).

We want to state that similar kinetics with stretched exponentials occur in some metallic or ceramic systems (melts, annealed materials, *etc.*) [28]. One may recall here a thickening process of very large plates or segregation of dislocations. We may suspect that the hydration process modelled in the work can be of civilian transformation type with non-glissile, coherent

or incoherent, interfaces of the swollen phases [28, 29]; *c.f.* [7] and refs. therein. One has to realize that certain concepts, borrowed from the studies of diffusion systems in which a response of material exerted by its elastic modulus changes is observed, may certainly be of help like in [30], where the hydrogen transport through metallic membrane was studied. Moreover, it should be stressed that a statistical self-similarity of the porous membrane material and the scaling behaviour permeability against porosity of a system under investigation have to be revisited and adapted to an elastic porous "tissue" (see [31] and references therein). A crucial point that is worth to address should account for the role of chemical reaction in a complex medium like biphasic mixtures, amphiphilic layers, systems with fluctuating barriers (*e.g.* biological materials), *etc.* Recent investigations in this area show that presence of memory effect in the system decreases the chemical reaction rate constant (*c.f.* [32] and references therein). Also, if a chemical reaction field affects a reactive medium one may expect not only some structural changes of it (some new chemical bonds and "bridges", like π bonds, can emerge), but one can observe that a certain tunning and stabilization of pattern formation is possible as well [33]. These general observations are in qualitative accord with our modeling.

Last but not least we wish to support the argumentation presented in this paper by invoking a study on protein channel kinetics (*i.e.*, which is the mechanism of channel opening and closing) presented in [34]. First, the authors used, qualitatively, the same kind of kinetic equation like in our study (Eq. (1) of the preceding chapter). Second, the 'kernel' of this equation was also of the same quality (*c.f.* Eq. (2) for details). Some subtle difference was that the exponent h that we have used was given by $h = 1 - D$, where D played the role of the fractal dimension of the protein channel [34]. The fractal-like kinetics was postulated there since during the passage of ions through the protein channels proteins conform to a huge number of the minimum energy conformational states, *i.e.* the process, like that described above, is 'suspected' to pass through many time domains. We see some analogies with the process studied in this work. Despite some details the most striking analogy would be that the channel closing ($D \to 2$) and opening ($D \to 1$) procedure is reminiscent of our kinetics of phase transformations between the squeezed ($\gamma = 1/3$) and elongated ($\gamma = 3/5$) lipid matter state, respectively.

Finally, we would like to express our hope that the problem will attract an increasing attention because of possible vast applications mentioned *e.g.* in [35]. A certain need for some new experiments, mostly leading to determination of h-exponent can be underlined as well. Also, one has to be aware or even cautious that the modeling offered here shows rather certain promissing trends towards a qualitative agreement between theory and experiment than

it gives somebody satisfaction from the very formal point of view. In other words, it means, that the general role of this study relies mostly on sketching some possibilities on how to attempt to deal with kinetics of the phase transformations in the model lipid membranes by combinig the well-known and rather ancient but still very useful AK-description with quite modern concept of the chemical reaction fractal-like kinetics since both of them suit very well the case modelled [36].

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