

Rapid Note

Nucleation-and-growth problem in model lipid membranes undergoing subgel phase transitions is a problem of time scale

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Received 30 November 1998

Abstract. In this *Rapid Note*, we show that the problem of growth of molecular superlattice in a fully hydrated dipalmitoylphosphatidylcholine (DPPC) membrane during the gel-to-subgel phase transformation process is a problem of time scale. There are, in fact, two time scales. The first is an “integrated” or, in some sense, stagnant time scale, that reflects the well-known isotropic growth effect in the d -dimensional space, but assigns the problem to be still in a category of Debye relaxation kinetics. The fraction of old (parent) phase does not suit the Paley-Wiener criterion for relaxation functions, and the time behavior is exclusively due to the geometrical characteristics of the kinetic process. The second (multi-instantaneous) time scale, in turn, is recognised to be a “broken” (fractional time derivative) or memory-feeling (dynamic) scale, which carries some very essential physics of the phenomenon under study, and classifies the problem to be of non-Debye (*viz.*, stretched exponential) nature. It may, in principle, contain all the important effects, like small scale coexistence, presence of collisions between domains, with possible annihilation and creation of domain boundaries, and/or a headgroup packing, hydration against lipid mobility behavior, and finally, a multitude of quasi-crystalline states. It turns out, that within the range of validity of the dynamic scale approximation proposed, the criterion for relaxation functions is very well fulfilled.

PACS. 82.60.Nh Thermodynamics of nucleation – 64.60.-i General studies of phase transitions – 64.70.-p Specific phase transitions

A recent comment [1], being a prompt response to some experimental study [2], showed that there is now experimental agreement that the gel-to-subgel phase transition kinetics in a fully hydrated dipalmitoylphosphatidylcholine (DPPC) model membrane is anomalous, and the agreement even extends to the surprisingly small numerical value of 1–1.3 for the effective dimensionalities of this phenomenon when interpreted in terms of Avrami-Kolmogorov (A-K) kinetics. However, both those, comment [1] as well as experimental study on the growth of molecular superlattice [2], noted that it is an outstanding problem how to understand this anomalous dimensionality theoretically.

The classical nucleation-and-growth mechanism, due to Avrami and Kolmogorov (and/or, Mehl Johnson, well-known, *e.g.* in physical metallurgy; *cf.* [1–4], and Refs. therein) of this and related [5,6] typically domain-wise [7] processes has been proposed to explain, in a simple quantitative way, the kinetic behavior of the transition. From those studies, it follows [1–4] that the subtransition depends upon the dimensionality d of the isotropic Euclidean or (possibly) non-Euclidean lipid spaces, but

under the experimental circumstances described [1,3], certain questions may arise, *e.g.*, whether that volume kinetics ($d = 3$) do accurately reflect the kinetics of the subtransition [2] or the process has to be reconsidered in terms of an isotropic growth with $d = 2$, or (perhaps) between $d = 3$ and $d = 2$, *i.e.* with some d , being even of noninteger value [4–6]? As we know (*cf.* [1–6], and Refs. therein) A-K theory predicts that the fraction of untransformed (parent) phase, $Y(t)$ (equal to $1 - X(t)$ in [1]), is going to decrease in the course of time as

$$Y(t) \simeq \exp \left[- \left(\frac{t'}{\tau_c} \right) \right], \quad (1)$$

where τ_c represents the characteristic (relaxation) time, and the time, in which the so-called “extended volume” [4–6] evolves, reads

$$t' = \int_0^t t_1^{d-1} dt_1 = \frac{1}{d} t^d, \quad 1 \leq d \leq 3, \quad (2)$$

which means, that, from the mathematical viewpoint, the only operation which has been performed, is a time scale augmenting (t^d), but this kind of transformation remains

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invariant under $t \rightarrow \text{const} \times t$, also for $d = 1$. (This is just exclusively a time variable expansion due to isotropic “geometrically controlled” as well as unimpeded growth [6]; note that if $d = 1$, then $t' = t$, exactly (see, Eq. (2)). Let us recall that this kind of (Debye or simple exponential) relaxation, explicitly given by (1) has, however, proved to be unphysical though very well applicable, since it does not fulfill the Paley-Wiener criterion, stating explicitly bounds for physically acceptable relaxation functions (for long times) [8], so that, as was expected [1,3], it does not reflect all the subtleness of the subtransition, since A-K theory is not really satisfying.

Thus, there is no doubt that we have to seek another way towards explaining the problems (inevitably related to the time scale [4]). It would be possible to do, if we realize that the nucleation-and-growth mediated transition is a time-dependent process that can be mapped onto a Random Walk (RW) of possibly anomalous character. (Some arguments have been provided, *e.g.* in [4,5], for the existence of a “sequential” mechanism, in which the transition is continuous throughout the system, which means, that a possibly continuous spectrum of metastable crystalline states is realized, or equivalently, a multi-instantaneous time scale seems to play a role.) To be more specific, let us notice that in our case, *i.e.* when the subgel transition is realized, one has to carry the system towards a lower temperature limit, which causes some apparent changes in the membrane structure and a certain loss of the number of the degrees of freedom for the individual macromolecules and their assemblies, even [2,4]. In the high temperature regime, in turn, one detects a well-intermingled (random) structure, with a maximum number of the degrees of freedom, where the existence of the molecular superlattice as well as the second [2] specific hydrocarbon chains’ sublattice, both of them being (more or less) commensurable and containing some respective amount of water penetrants, are easily observed. When lowering the temperature, the structure goes to a regime of sol-like phase, in which some discontinuities due to lesser mobility of hydrocarbon chains as well as caused by water dehydration appear [3,5]. In the correspondence to what has been written above, one may expect that above the temperature (percolation) transition point, the dynamics is well described by the normal (linear) RW as well as the Debye (simple exponential) kinetics. At the transition point (and slightly below), however, because of some appearance of the above mentioned constraints, such a description is no longer valid, since one has practically to do with much slower dynamics, being presumably described in appropriate way by means of the anomalous (subdiffusive) RW and the non-Debye kinetics corresponding to it [6,8,9]. Since the process is realized in a domainwise manner, one can think of the realization thereof either in a naive or in a formal (more focused) way. In the former, we have to accept that the process relies on, say, annihilation and creation of domains and their boundaries (typically, the bigger grains “eat” the smaller ones, which is often subjected to a grain-boundary free energy (curvature driven) decrease mechanism; *cf.* [6], and Refs. therein), so

that it resembles a motion of randomly hopping walker. In the latter, we have to make use of a similarity of the problem in question, solved in a space of the grain (domain) boundary area (which is a stochastic variable; see also a metallurgical example therein [6,7]), and a problem of randomly walking tracer in its position space. This problem is called the anomalous Random Walk problem in the standard literature (see [9], and Refs. therein) and seems to be well elaborated.

The tissue recalled is also quite well understood for the gel or gel-like phases, and it is generally located in a class of (dynamic) percolation problems, so that a Random Walk on the percolation (Swiss-cheese-like structure) must be invoked. A solution of the problem leads to have an “excess quantity”, say Δ , which makes a difference between a normal and anomalous RW-s, since the former is realised in an isotropic (well-mixed or sufficiently intermingled) collision space, whereas the latter proceeds on a more crumbled substrate. In this case, the mean-squared displacement $\langle x^2(t) \rangle$ of a RW-particle is found to scale with (arbitrary) time variable t as

$$\langle x^2(t) \rangle \sim t^{2/2+\Delta}, \quad t \gg 1, \quad (3)$$

but preferentially at the subgel transition point, since above it one provides a standard RW problem solution, like $\langle x^2(t) \rangle \sim t^1$ [10]. Here, Δ , where $0 < \Delta < 1$ (also) contains typically all the basic continuous phase transition characteristics for the percolation (gel phase formation) process, *i.e.* the process which is a transition between an infinite incipient cluster and some finite clusters containing phase (the transition process resembles to some extent the paramagnetic-ferromagnetic phase transition, but is equally well assigned to the gel-sol phase change; *cf.* [3] for a verbal picture of the subtransition, which seems to be very much consistent with the argumentation presented above). By the way, bear in mind that an exponent, d_w , where $d_w = 2 + \Delta$, is usually named the fractal dimension of RW, and because $d_w > 2$, the anomalous RW is said to be subdiffusive or anomalously slow [10].

For such a system, the subdiffusive RW kinetic phenomenon is equivalent to a fractional relaxation process of order $0 < \delta < 1$ (*cf.*, [7], and Refs. therein), where $\delta = \frac{1}{1+(\Delta/2)}$ (see relation (3), too), so that the corresponding relaxation equation can be written as [11]

$$Y(t') + \tau_{ca} \frac{d^\delta}{dt'^\delta} Y(t') = 0, \quad (4)$$

where τ_{ca} is recognized to represent another characteristic relaxation time, proportional to τ_c , and $\frac{d^\delta}{dt'^\delta}$ stands for a fractional time derivative, given by the Weyl’s integral operator (*cf.* [12] for mathematical details). Notice, that if δ were equal to 1, then (4), being of the form $Y(t') + \tau_{ca} \frac{d}{dt'} Y(t') = 0$, would produce a “classical” Debye solution of type (1, 2). (In general, one has $\delta \leq 1$, however. It is necessary to stress, perhaps again, that if $\delta < 1$, one recognizes a subdiffusive RW, which corresponds to the non-Debye relaxation process. Otherwise, *i.e.* when $\delta = 1$ one gets the “normal” RW.)

The most important thing is, that now the asymptotic solution of (4) is not a simple (*viz.*, Debye) exponential, but a stretched (*i.e.*, non-Debye) exponential of the form, namely

$$Y(t) \simeq \exp \left[- \left(\frac{t'}{\tau_{ca}} \right)^\delta \right], \quad (5)$$

where t' is given by (2). In general, the solutions of (4) belong to a class of Mittag-Leffler functions [11,12], *i.e.* they obey very well the Paley-Wiener criterion [8]; specifically, they are either stretched exponentials or algebraically decaying time variable functions [8,11]. Solution (5), formally taken with (2), apparently changes possibilities of interpretation(s) of experimental results obtained [1–5] because, at the transition point, and perhaps slightly below, the effective and readily fractional dimensionality is not d , being typically of integer value (see Eqs. (1, 2)), but δd . For example, now, one should be able to elucidate, why the effective dimensionalities of the subtransition in DPPC are about 1–1.3, or other dimensionalities measured for some prerequisites of lyotropic liquid crystals (and polymorphic [2,4,6] phase transformations customarily assigned to them) [4,5] can even be less than one. Namely, notice, that if, *e.g.*, one may have $d = 2$ [1–5], and if one reasonably assumes that a maximum value of δ becomes $\delta \approx 2/3$ [9,10], then one can get $\delta d \approx 1.333$, which approaches quite well the measured maximum value of 1.3 mentioned in [1–3]. There are, however, theoretical and experimental evidences [9,10,13], that mostly for 2d (order-disorder, in particular, solidification *vs.* melting) systems, Δ can exceed one, *i.e.* $\Delta > 1$, so that in principle, a value of δd less than 1.3, or even being (apparently) smaller than or, at most, equal to one can probably be reached (even, if $d = 3$ will be taken).

Another problem, however, remains. It concerns now a technical possibility as well as reliability of measuring Δ (recall that $\delta = \frac{1}{1+(\Delta/2)}$), which is usually expressed by the (standard) critical exponents β, ν and μ (*cf.* [6, 10]) of the percolating or, in particular, gelling systems [10]. It can be shown quite rigorously, that $\Delta = \frac{\mu-\beta}{\nu}$, where μ, β as well as ν can be taken from basic scaling relations, characterizing the gelling system near criticality, when an infinite 'spanning' cluster may be formed [9,10]. The issue of measuring the critical exponents μ, β as well as ν [10] can be addressed to experimentalists, who would, hopefully, pick up them for their systems that they wish to investigate.

In a final word, let us notice that a result, qualitatively similar to (5), can be recovered, when one presumes the standard A-K description of the subtransition [2], but in terms of the fractal-like ("long-tail") kinetics [9], *i.e.* with the kinetic coefficient being inverse powerly time-dependent; *cf.* [6] for details. Although in [6] no very well-argued microscopic picture of the process was offered, it seems to be in a striking conceptual agreement, *e.g.* with findings of Tenchov *et al.* [4].

A support of the Polish State Committee of Scientific Researches is mentioned. The author wishes to thank J.F. Nagle for discussions.

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