Available online at www.sciencedirect.com

ScienceDirect

Physica A 387 (2008) 3511–3525

PHYSICA A

www.elsevier.com/locate/physa

Theory of lateral and flip-flop phase separations in bilayer biomembranes and surfactants

M. Benhamou[*], M. Ouarch, H. Kaidi, M. Chahid

Laboratoire de Physique des Polymères et Phénomènes Critiques, Faculté des Sciences Ben M'sik, B.P. 7955, Casablanca, Morocco

Received 25 March 2007; received in revised form 6 November 2007
Available online 19 February 2008

Abstract

In this work, we consider bilayer biomembranes or surfactants made of two amphiphiles A and B. Under a variation of a suitable parameter, such as temperature or difference of lengths of hydrophobic chains, these systems undergo a phase separation from a homogeneous liquid-phase to two distinct liquid-phases. Two physical situations can be distinguished: (1) The amphiphiles A and B prefer to jump from a monolayer to the other (*flip-flop* transition), (2) the mixture phase separates on each monolayer, and there is no jump from one sheet towards the second one (*lateral* transition). To investigate the associated critical phase behavior, we first introduce a field theory, constructed with two order parameters (or fields) φ and ψ, which are nothing else but the composition fluctuations relative to the monolayers. Beside the usual terms proportional to φ^2, ψ^2, φ^4 and ψ^4, the free energy contains an extra one, $-C\varphi\psi$, which describes the lowest order coupling between the two monolayers. The coupling constant C is positive for the lateral phase separation, and negative for the vertical one. We show that its sign results from a competition between the chemical segregation of amphiphiles and the curvature asymmetry. With the help of this free energy, we first identify the liquid-phases, and show the existence of a critical point, T_c, of which the location depends naturally on the value of the coupling constant C. In particular, for those bilayer biomembranes or surfactants made of amphiphiles of the same chemical nature but with different lengths, and at fixed temperature, we show the existence of a critical line in the $(\Delta c_0, \Delta l)$-plane, along which the bilayer undergoes a phase separation. Here, Δc_0 and Δl account for the curvature gap and the length difference, respectively. Second, we determine the behavior of the composition fluctuations, φ and ψ, and the total one, $\Phi = \varphi + \psi$, upon temperature, T, and chemical potential difference, $\Delta\mu$, in the critical region. Third, we determine the critical behavior of the partial compressibilities, $\kappa_{\varphi\varphi}$, $\kappa_{\psi\psi}$ and $\kappa_{\varphi\psi}$, and the overall one, $\kappa_{\text{tot}} = \kappa_{\varphi\varphi} + \kappa_{\psi\psi} + 2\kappa_{\varphi\psi}$. Finally, we remark that the flip-flop phase separation shows some analogy with the classical para-ferrimagnetic transition of coupled paramagnetic materials of Curie–Weiss type.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Biomembranes; Surfactants; Lateral and flip-flop phase separations; Phase behavior

---

1. Introduction

For more than three decades, the structure and functions of biological membranes have been the subject of intensive investigations. The idea that the biological membranes present as lipidic bilayers is now largely recognized

---

[*] Corresponding author. Tel.: +212 22 70 46 75; fax: +212 22 70 46 75.
E-mail address: m.benhamou@univh2m.ac.ma (M. Benhamou).

0378-4371/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.physa.2008.02.032

by the scientific community. Contrarily to other covalent biological constituents (polynucleotides, proteins and polysaccharides), the bilayer is a self-assembly of non-covalent lipid molecules, which undertake free movements. Indeed, a lipid molecule can produce a movement on the surface of the two monolayers, called "lateral diffusion" [1]. Also, the molecule can jump from a monolayer towards the other – a transversal displacement termed "'flip-flop diffusion". Under certain conditions, the molecule can leave the lipidic bilayer. Finally, a lipid molecule may experience a rotational motion around its principal axis (rotational diffusion). Thanks to the lateral and rotational diffusions, the lipidic bilayer has the properties of a two-dimensional liquid, but the hydrophobic chains keep their parallelism and remain perpendicular to the surface of the membrane. This order resembles that usually encountered in liquid-crystals context. In summary, we can say that the membrane properties are largely determined by the nature of motion of its lipidic components.

The fact that the interaction forces between amphiphiles are relatively small favors their statistical distribution within the bilayer membrane. The formation of domains determine the properties of the biomembranes. There exists at least two kinds of immiscibility: (a) the lipid molecules aggregate and form domains (*lateral* phase separation); (b) the opposite monolayers of the bilayer may have different composition (*transversal* phase separation). The two processes occur within natural systems, such as cells and vesicles. The mechanism of the formation of domains is similar to the usual phase separation, caused by a change of temperature, ionic force, lateral pressure, and so on. Also, the integration of a molecule in the bilayer may favor a rearrangement of lipid molecules in domains.

The lateral phase separation may take place in the presence of ions (Ca^{+2}, for example), around an incorporated macromolecule or when the temperature is varied [2]. The vertical phase separation can be induced by an adsorption of a convenient polymer [2]. In fact, different interactions govern the phase separation mechanism, namely the forces between polar heads and between lipidic chains. For instance, a variation of the external pH allows a change of the charge of the polar head. This leads to a reduction of the attractive forces between two neighboring polar heads. The ions can also give rise to a redistribution of lipid molecules, because of the formation of complexes between polar heads and metallic ions. The adsorption of ionic polymers may increase the density of lipid molecules, which experience attractive electrostatic interactions. Similarly, the forces acting principally within the hydrophobic region of the lipidic bilayer may induce phase separations. For example, a change of temperature can lead to a phase separation of two lipid species of different melting temperatures.

The separation transition may occur even when there are small variations of the lipidic structure. A classical example is provided by the mixtures of phosphatidylcholines, when the acyls chains have different lengths. In this case, the polar heads are identical but the different lengths provoke segregation forces between unlike chains. Knoll et al. [3] and Silvius et al. [4] have studied the phase diagrams by varying progressively the length of chains. The authors were found that the phase separation produces when the difference between the lengths of acyls chains is four groups CH_2 or more. The first considered mixture was DLPC (C_{12})/DPPC (C_{16}). Experiment has shown that there is a distinct immiscibility in the gel phase leading to a solid/solid separation, in the interval 60 to 100 mol% DPPC, and the two solid phases coexist between 0 and 60 mol% DPPC. There is a complete miscibility at liquid state, with coexisting phases between the melting temperatures $T_{M,A}$ and $T_{M,B}$, in all composition range. The same tendency was found for the DMPC (C_{14})/DSCP (C_{18}) mixture, where the lengths of lipid molecules are augmented by two supplementary unities CH_2. The coexistence region between the liquid phases and solids form domains that can be detected by many experimental techniques. The sizes of these domains vary between several nanometers to several micrometers. These same domains may contain from 100 to more than 100 000 lipid molecules. Other experiments, in relation with the subject, appear in Refs. [5–7].

In this paper, we aim at a quantitative investigation of the lateral and flip-flop phase separation. We start with a lipidic bilayer composed of two kind of lipid molecules A and B. Under a variation of some parameter, the mixture undergoes lateral or vertical phase separations. Here, we restrict ourselves to the domain of relevant parameters where one assists to a liquid–liquid phase separation. Thus, this work is not concerned with solid–solid transitions.

To this end, we first propose a new theory that allows a consistent description of the demixing transition. This theory is constructed from two scalar fields φ and ψ that are the composition fluctuations (*order parameters*) relative to the monolayers. The parameters of the problem are the effective segregation parameters on monolayers and in between. The obtained free energy enables us to study the critical phase behavior. First, we identify the liquid-phases and show the existence of a demixing critical temperature. Second, we study the behavior of the composition fluctuations upon temperature and chemical potential difference. Finally, we determine the partial and total compressibilities versus temperature, near criticality.

Download English Version:

https://daneshyari.com/en/article/974943

Download Persian Version:

https://daneshyari.com/article/974943

Daneshyari.com