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Helfrich's concept of intrinsic force and its molecular origin in bilayers and monolayers☆

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ABSTRACT

Bilayers and monolayers are excellent models of biological membranes. The constituents of the biological membranes such as lipids, cholesterols and proteins are chiral. Chiral molecules are abundant in nature (protein, nucleic acid and lipid). It is obvious that relationship between chirality and morphology (as well as function) of biological membrane is of interest for its fundamental importance and has technological implication regarding various membrane functions. The recent years have witnessed that a number of experimental studies in biomimetic systems have shown fascinating morphologies where chirality of the constituent molecule has decisive influence. Significant progress is made towards the understanding of these systems from the theoretical and computational studies. Helfrich's concept of intrinsic force arising from chirality is a milestone in understanding the biomimetic system such as bilayer and the related concepts, further progresses in molecular understanding made in recent years and experimental studies revealing the influence of chirality on morphology are the focus of the present review. Helfrich's concept of intrinsic force arising due to chirality is useful in understanding two-dimensional bilayers and one-dimensional monolayers and related mimetic systems. Various experimental techniques are used, which can probe the molecular architecture of these mimetic systems at different length scales and both macroscopic (thermodynamic) as well as microscopic (molecular) theories are developed. These studies are aimed to understand the role of chirality in the molecular interaction when the corresponding molecule is present in an aggregate. When one looks into the variety of morphologies exhibited by three-dimensional bilayer and two-dimensional monolayer, the later types of systems are more exotic in the sense that they show more diversity and interesting chiral discrimination. Helfrich's concept of intrinsic force may be considered useful in both cases. The intrinsic force due to chirality is the decisive factor in determining morphology which is explained by molecular approaches. Finally, biological and technological implications of such morphological variations are briefly mentioned.

Contents

1. Introduction

Membranes are tremendously important biological systems and are absolutely essential for all live being on earth. They encapsulate the content of cell and maintain a chemical structure within the cell that differs from the extracellular region. Membranes allow selective passage of atoms, molecules and ions through channels exhibiting a selective permeability. Recognition processes in membranes are extremely important due to their biological relevance. Example is the recognition by receptor proteins present in membranes composed of lipid molecules. It is no wonder that the structure and properties of membranes and their models (membrane mimetic systems) such as bilayers and monolayers are subject of intensive studies over several decades. Membranes are generally composed of lipid molecules or similar amphiphiles which

☆ This review is dedicated to Professor Wolfgang Helfrich on the occasion of his 80th birthday.

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have both hydrophobic and hydrophilic character. Other principal components of membranes are functional biological molecules such as proteins and carbohydrates embedded in membrane. Various types of lipids such as, fatty acids, esters of fatty acids (acylglycerolic and phospholipid amphiphiles), isoprenoids (sterol, sterol esters) and glycolipids are present in cell membranes. The core part of the membranes is a bilayer composed of amphiphiles, which is the matrix of all biological membranes. Membrane structure is inherently complex (multi-component with exotic properties). Due to the complex structure and dynamics of membranes, often simpler bilayers and monolayers composed of amphiphiles are used as simpler model systems. Amphiphilic bilayer and monolayer are examples of membrane mimetic system (Fig. 1). Despite the simplicity of these model systems, bilayers and monolayers exhibit interesting morphology which sheds light on the physicochemical forces and factors controlling the membrane structure, dynamics and function. The diversity of the phase, morphology and functionality made the understanding of membranous systems challenging. Membrane and membrane mimetic systems are self-aggregated systems. The principal favorable component of the free energy of aggregation is the hydrophobic effect and the repulsive component is the electrostatic head group repulsion. A balance between the two factors (along with other components of free energy such as the loss of translational and rotational degrees of freedom of the amphiphiles and entropic effects) is responsible for the formation of the finite aggregates.

Bilayers and monolayers are excellent models of biological membranes. The constituents of the biological membranes such as lipids, cholesterols and proteins are chiral. Chiral molecules are abundant in nature (protein, nucleic acid and lipid). It is obvious that relationship between chirality and morphology (as well as function) of biological membrane is of interest for its fundamental importance and has technological implication regarding various membrane functions. Recent years have witnessed that a number of experimental studies in biomimetic systems shown fascinating morphologies where chirality of the constituent molecule has decisive influence. Significant progress is made in this direction from the theoretical and computational studies. Helfrich's concept of intrinsic force arising from chirality is a milestone in understanding the biomimetic system such as bilayer. It is pointed out by Helfrich that when chiral molecules are present in succession in a row in a bilayer, twists along the rows in a right-handed sense (or clockwise) are present and the resulting morphology is non-superimposable over the morphology resulting from twist in left-handed (anti-clockwise) sense and this is due to the intrinsic molecular chirality. A collective tilting may lead to an anisotropic curvature and this may occur when molecules are chiral. The related concepts, further progresses in molecular understanding made in recent years and experimental studies revealing the influence of chirality on morphology are the focus of the present review.

It is well known that the finite shape of amphiphilic aggregate is controlled by the balance between the attractive forces (such as hydrophobic interaction between the alkyl chains, weak van der Waals type interactions between amphiphile molecules within the aggregates) and repulsive forces (such as electrostatic repulsion between head groups, reduction of translational and rotational degrees of freedom of the amphiphile). The shapes of various amphiphilic aggregates such as spherical micelles, and bilayers are explained in terms of the balance of forces and empirical packing parameters essentially representing short-range repulsion and long-range attraction [1]. Similar semi-microscopic approaches to explain the aggregation phenomena predicted several features of various amphiphilic aggregates [2]. The major limitation of such approaches is that they rely on a number of parameters. Over the last few decades, it is understood that factors other than hydrophobicity or electrostatic head group repulsion play a major role in determining the aggregate structure of systems composed of amphiphiles. Recent results on the morphology of monolayers and bilayers using fluorescence, Brewster angle microscopy and Grazing incidence X-ray diffraction analysis posed further challenges in developing a complete understanding of the morphologies of various phases of amphiphilic aggregates [3–8]. Varieties of bilayer and monolayer aggregate shapes are revealed by these techniques [5–9] and these new results pointed towards the fact

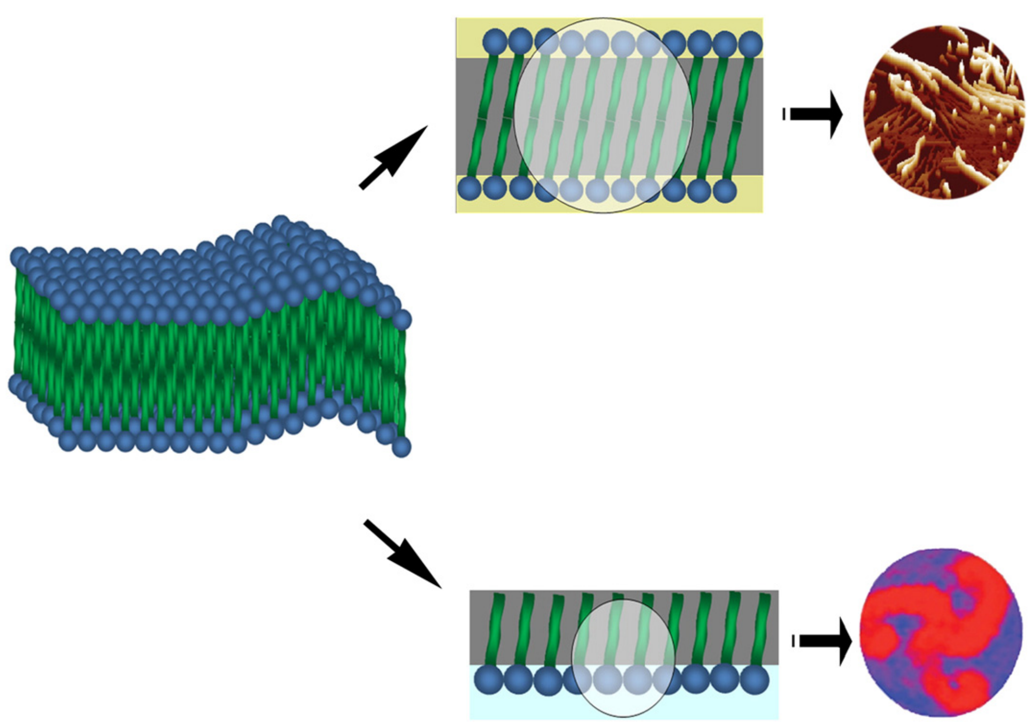

Fig. 1. Schematic representations of the segment of a membrane and its two mimetic systems such as bilayers and monolayers, respectively. The curvature of the membrane composed of chiral molecules is a manifestation of the anisotropic forces in which intrinsic bending force is an important component. Two representative mesoscopic structural organizations of bilayers (Langmuir–Blodgett film) and monolayers (domain in Langmuir monolayer) are shown at the right hand side. The curvature or handedness of the domain at air–water interface for example, is driven by intrinsic force originating from molecular chirality.