

Entropic driven self-assembly of nonamphiphilic colloidal membranes

Proc. Natl. Acad. Sci. USA **107** (2010) 10348.

Edward Barry and Zvonimir Dogic

Recommended with a commentary by Thomas R. Powers, Brown University

Since the controlled assembly of nanostructured materials remains a major challenge, we often turn to biological systems for inspiration. For example, the lipid molecules found in cell membranes are amphiphilic, with oily hydrophobic tails and polar hydrophilic head-groups. In water, lipids self-assemble bilayer membranes a few nanometers thick, with the tails hidden from the water behind the heads [1]. Non-biological amphiphilic molecules such as block copolymers self-assemble artificial membranes by the same principle [2]. In their recent article [3], Barry and Dogic describe how to self-assemble monolayer membranes in solution in a way that relies on the geometry of the constituents, rather than the amphiphilic property. Again, biology plays a crucial role: the membranes are composed of *fd* viruses, stiff rod-like particles ≈ 880 nm in length and ≈ 7 nm in diameter.

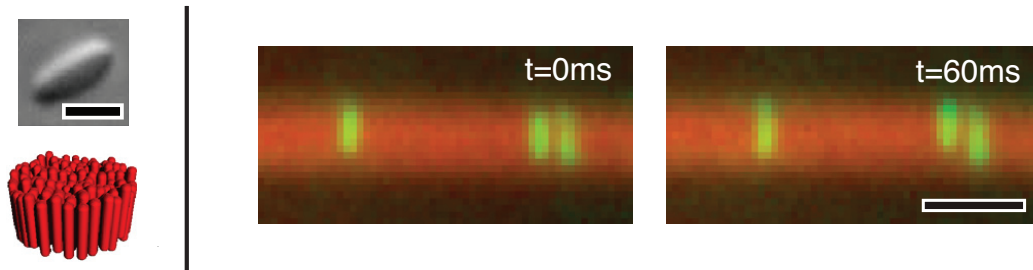


Figure 1: Left panel: DIC micrograph (above) and schematic (below) of disks formed from self-assembled *fd* virus particles. Right panel: Polarization and fluorescence images superposed to show a membrane (red), viewed edge-on, and individual fluorescently-labeled virus particles (green) at two different times. Both scale bars are $2\ \mu\text{m}$. Figure adapted from [3].

These colloidal membranes form due to attractive interactions between the viruses induced by the depletion effect. Since the viruses are hard particles, their configuration is governed by entropy. The solution contains the polymer Dextran along with the viruses. The polymer acts as the depletion agent: when two viruses come close enough to each other that no polymer particle can squeeze between them, then the volume available for the polymers to explore increases, leading to an increase in entropy and decrease in free energy, and thus an attractive interaction [4]. Barry and Dogic observe that the formation of the final structures occurs in two steps. First, the rods aggregate to form disks (left panel, Fig. 1). At high polymer concentrations, the disks stack and form filaments. The aggregation of the disks can again be understood as a consequence of the depletion interaction. But at low polymer concentrations, there is a surprise: the disks do not stack, but instead coalesce to form larger and larger disks—membranes. Why doesn't the depletion interaction cause these membranes to stack into layered structures?

To answer this question, Barry and Dogic exploit the fact that fluctuations of individual virus particles and the bending fluctuations of the membrane can be visualized simultaneously. The right panel of Fig. 1 shows individual virus particles (green) viewed in fluorescence along with a polarization image of the membrane (red), which reveals that individual rods occasionally protrude from the membrane. The membranes are rough at the scale of the virus particles. If the membrane is sufficiently rough, then the volume available to the polymers does not increase as two membranes approach each other, since the membranes cannot fit together smoothly. A similar suppression of the stacking of disks has been observed in disks with fixed bumps [5, 6]. In the system of Barry and Dogic, there is also an entropic cost for pushing two membranes against each other, since that would limit the number of protrusions. Thus, the protrusions lead to an effective repulsive interaction, which has also been studied in lipid systems [7]. This repulsive interaction stabilizes the free membranes at sufficiently low polymer concentration. Note that the range of the attractive depletion interaction depends on the size of the polymer but not the concentration. The range of the repulsive interaction depends on polymer concentration, since as the concentration increases, the heightened osmotic pressure suppresses protrusions.

Despite the non-amphiphilic nature of the rods, the colloidal membranes have properties similar to those of lipid bilayer membranes. The membranes are fluid, and display bending and area fluctuations that can be used to determine the bending and compression moduli. Thus, the colloidal membranes should prove to be useful model systems for improving our understanding of their smaller counterparts.

References

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