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Title
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In PNAS, Freund (1) analyzes the problem of the entropic interactions between flexible lipid bilayer membranes at both small and large separations. A main conclusion is that, over a large range of separations, the repulsive force essentially varies with the inverse of the separation, c^{-1}, between the membranes (bilayers), in marked contrast to the current consensus in the literature. In this letter we point out three important issues that Freund does not consider in his report.

At small bilayer separations, one experimentally finds an exponentially repulsive force that depends strongly on separation, with a characteristic decay length of 0.2–0.3 nm. The molecular origin of this repulsion has been extensively discussed, and in agreement with Freund's approach, we have previously argued that the basic cause is entropic (2). However, one has to go beyond the harmonic approximation used by Freund to obtain a result that is reasonably realistic, especially at separations approaching molecular sizes where it is necessary to have a molecular description of the interaction.

Freund considers the model where the bilayer is mapped onto a surface with bending modes. This consideration is essentially the same as previous continuum treatments of the "undulation force" at long range, which was first done by Helfrich (3). In such a model there is asymptotically only a single length-scale—the inverse area per unit volume, V/A—whereby the configurational integral is invariant under a length-scale transformation. This finding implies that the solvent chemical potential, and thus the force, varies as c^{-3} (4), a result that is obtained without an explicit evaluation of the partition function.

The third issue concerns experimental characterizations of the undulation force. In his report (1), Freund discusses experimental determinations of the force based on Caillé effects in diffraction experiments. This is a somewhat indirect method for determining interaction forces and, as Freund points out, does not provide a precise measure of the distance dependence of the force. The undulation force is relatively weak, putting high requirements on the accuracy of direct measurements. This finding is particularly true for phospholipid bilayer systems, which have a relatively high bending rigidity. However, there are surfactant systems that readily form bilayers with bending rigidities that are an order-of-magnitude smaller. Together with colleagues, we have determined the force distance relation for such systems using two different methods for directly measuring the forces. Bagger-Jörgensen and Olsson* used the osmotic stress technique to measure the force in a nonionic surfactant system for 15 samples in the "long-range" distance regime from 9 to 25 nm. The data are in excellent agreement with a c^{-3} dependence of the force and clearly incompatible with a c^{-1} dependence. Similarly, Bulut et al. (5) applied a centrifugal force field to a non-ionic bilayer system, where the observed concentration profiles provide a direct measure of the force-distance relation. These experiments also clearly showed a c^{-3} dependence of the force, as predicted by Helfrich (3) in his original, pioneering work.

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1 Freund LB (2013) Entropic pressure between biomembranes in a periodic stack due to thermal fluctuations. *Proc Natl Acad Sci USA* 110(6):2047–2051.
2 Israelachvili JN, Wennerström H (1992) Entropic forces between amphiphilic surfaces in liquids. *J Phys Chem* 96(2):520–531.
3 Helrich W (1978) Steric interaction of fluid membranes in multilayer systems. *Zeitschrift für Naturforschung* 33(3):305–315.
4 Wennerström H, Olsson U (1993) On the flexible surface model of sponge phases and microemulsions. *Langmuir* 9(2):365–368.
5 Bulut S, Åslund I, Topgaard D, Wennerström H, Olsson U (2010) Lamellar phase separation in a centrifugal field. A method for measuring interbilayer forces. *Soft Matter* 6:4520–4527.