(wavevector, **k**) and its energy (frequency, ω) — for a metal/air interface is given by the solid line in Fig. 1. The important thing to notice about this is that with increasing energy/frequency, this relation hits an asymptotic limit. The position of this limit depends not only on the properties of the metal, but also on the refractive index of the medium on which it rests. The dotted curve shows how a material of higher refractive index than air, such as the InGaN used in the LED experiment, alters the dispersion relation to lower this asymptotic limit from ω_{air} to ω_n. Moreover, because the density of SPP states is inversely proportional to the slope of the dispersion relation, this density reaches a maximum as the asymptotic limit is approached. Consequently, by selecting a metal so that the asymptotic limit for SPPs falls close to or within the emission band of the semiconductor, the coupling between excitons and SPPs — and therefore the chances that the former will decay into the latter — can be increased. And by combining this with a rough metal interface to scatter the resulting SPPs to produce photons, the luminescent efficiency can be enhanced.

The idea of arranging the asymptotic limit of the SPP dispersion relation to be within the emission band of a semiconductor has been proposed before, but the present work is the first to demonstrate that it can be used effectively. This demonstration relies on the very high refractive index of the inorganic semiconducting materials ($n \approx 2.5$) to bring the asymptotic limit into the visible part of the spectrum. For lower-index light-emitting materials, such as the conjugated polymers, is it possible recent developments in surface metamaterials may offer a similar route to SPP-engineering efficiency enhancements — though at this stage such possibilities are very speculative.

Although the results reported at this stage are preliminary — Okamoto *et al.* demonstrate enhancement of the photoluminescence of an optically pumped multilayer device, rather than an electrically pumped LED — they do offer the possibility of turning what might initially be perceived as a problem (losses to surface plasmon-polariton modes) into an advantage. Whether it proves to be a commercially viable proposition remains to be seen, but regardless, it certainly adds a fascinating extra dimension to the exploration of surface plasmon-polariton related phenomena along the road to ultra-efficient LEDs.

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BIOMIMETIC MEMBRANE MODELLING
Pictures from the twilight zone

Biological and biomimetic membranes are multiscale assemblies extending from small molecular clusters to large domains with an area of 100,000 nm^2. New computer simulations give us a look into this experimental twilight zone.

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Biological and biomimetic membranes such as those surrounding cells and vesicles are very thin bilayers that have rather unusual materials properties. They are both highly flexible and robust, able to adapt their shape and keep their structural integrity even when they undergo relatively strong deformations, such as those that occur when cells are squeezed through narrow capillaries. Understanding the structure and dynamics of these membranes is very challenging because they are truly multiscale structures that involve many levels of self-organization. Spectroscopic methods have been used for many years to probe the local neighbourhood of single membrane molecules, but these methods cannot give information about lateral membrane domains that contain more than a few such molecules. During the past couple of years, it has become possible to observe large domains — exceeding half a micrometre in diameter — by light microscopy[1] (as recently discussed at the workshop on *Membrane Rafts*, Newton Institute, Cambridge, UK, 19–20 May 2004). Nevertheless, there is still a large experimental twilight zone that extends from small membrane domains with an area of a few square nanometres up to relatively large domains with an area of 100,000 nm^2. Computer modelling and simulations have become very valuable tools to probe this intermediate twilight zone. Using coarse-grain molecular dynamics simulations, Goundla Srinivas, Dennis Discher and Michael Klein
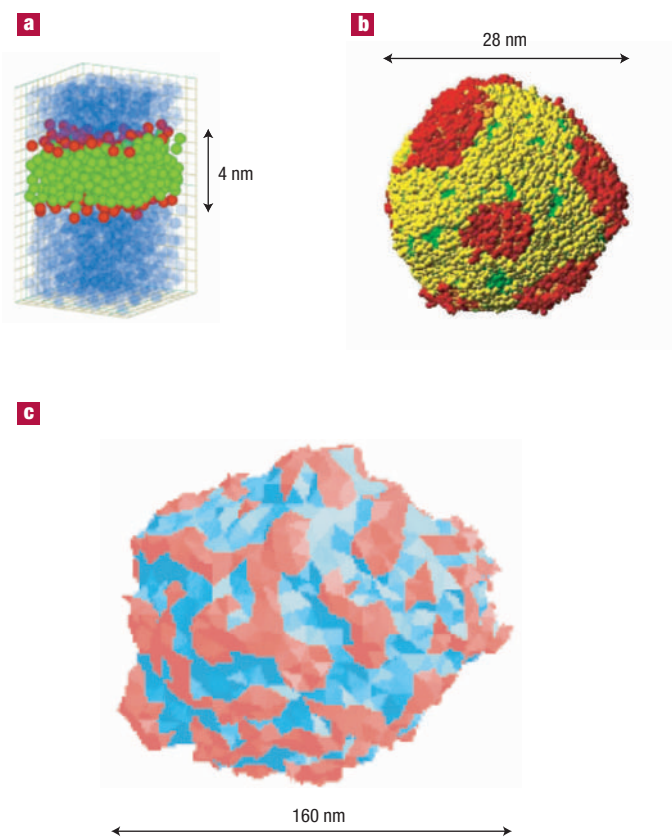
the molecules can flow within the membranes and undergo rapid lateral diffusion in the absence of external forces. Fluid membranes are easy to bend, and thus undergo a variety of shape transformations. One particularly interesting example is provided by the formation of small spherical buds, a process that leads to exo- and endocytosis of biological cells, and which is essential for the intracellular traffic of vesicles.

Starting in the 1980s, various simulation codes have been developed in order to study 'all-atom' models for bilayer membranes. These models give detailed information about the conformations of the amphiphilic molecules and their interactions with water. However, because these all-atom simulations are computationally quite demanding, they are limited to relatively small membrane patches, which have an area up to 200 nm^2, and to relatively short time scales (up to 100 ns). In order to simulate larger bilayer patches for longer times, one must use 'coarse-grain' models, in which groups of atoms are combined into effective particles or beads (Fig. 1).

In general, the study of coarse-grain models can serve two different and complementary purposes (as discussed at the workshop on *Self-Organization in Biomolecular Systems*, Centre Europeen de Calcul Atomique et Moleculaire, Lyon, France, 22–24 October, 2003). On the one hand, these models can be used in order to gain further insight into conceptual issues, such as the nature of bilayer states, which are essentially tensionless, and the bending rigidity of these membranes[4]. On the other hand, they can be applied to specific membranes that are built up from certain types of bilayer-forming molecules. In the latter case, one has to make a careful choice of model parameters. During the past couple of years, several procedures have been pursued in order to optimize this parameter choice by explicit comparison with thermodynamic data, experimental diffusion coefficients, and all-atom simulation data[5].

Klein and colleagues apply such a procedure to diblock copolymer bilayers[2]. Each diblock copolymer consists of one hydrophilic and one hydrophobic segment. The relative length of the hydrophobic and hydrophilic segments represents one important control parameter that determines the overall supramolecular organization arising from the self-assembly of the amphiphilic diblocks. Bilayers are formed if the hydrophilic/hydrophobic length ratio is sufficiently small. Another important control parameter that determines the thickness of the bilayers is the molecular weight of the diblocks for fixed hydrophilic/hydrophobic ratio. The simulations show that the hydrophobic copolymer segments within different leaflets of the bilayer become more and more entangled as one increases the diblocks' molecular weight. This entanglement and interdigitation leads to a nonlinear increase of the bilayer thickness with molecular weight, in good agreement with experimental data[6].

There are many more aspects of biomimetic membranes for which simulations of coarse-grain models will provide valuable insight. Two of these aspects are the lateral organization of membrane domains in the nanometre regime and the 'cold' fusion of membranes and vesicles. Membranes that contain

Figure 1 Snapshots of membranes and vesicles as obtained from different coarse-grain models and simulation algorithms. **a**, Molecular dynamics simulation of oriented bilayer segment containing 100 amphiphilic molecules. The hydrophilic head groups and the hydrophobic chains of these molecules correspond to the red and green beads, respectively; the water beads are blue. The bilayer segment has a thickness of 4 nm and a lateral extension of 6 nm. Reprinted image with permission from ref. 4. Copyright (1999) by the American Physical Society. **b**, Dissipative particle dynamics of a closed vesicle containing about 6,500 molecules. The membrane is composed of two types of molecules that have red and yellow head groups, respectively. The aqueous solution is modelled by beads as in (**a**) but is not shown. The vesicle has a diameter of about 28 nm. **c**, Monte Carlo simulations of a vesicle surface consisting of 1,200 red and 1,200 blue triangular membrane patches. The aqueous solution is not included in these simulations. The diameter of the vesicle is about 160 nm.

have successfully modelled diblock copolymer bilayers, which mimic much of the behaviour of lipid membranes[2]. The results suggest that computer modelling and simulation provide a rational design tool for the synthesis of novel block-copolymer architectures.

The unique combination of flexibility and robustness displayed by biological and biomimetic membranes arises from their supramolecular organization. These membranes consist of amphiphilic molecules, which are composed of both hydrophilic and hydrophobic parts that self-assemble into a variety of supramolecular structures. Some amphiphilic species such as lipids or diblock copolymers form unilamellar vesicles — closed 'bags' of single bilayers, which have a linear size between 30 nm and 100 μm (ref. 3). The flexibility of bilayer membranes and vesicles is intimately related to their fluidity, which implies that

several molecular components should undergo phase separation and form intramembrane domains. If the membrane is under low tension, these domains tend to form spherical membrane buds, a theoretical prediction[7] that has been recently confirmed by optical microscopy[1,7]. Where direct observation by optical microscopy is not possible, a variety of coarse-grain membrane models (Fig. 1) can be used to study bilayers containing several lipid or diblock copolymer components, or even mixtures of lipids and diblocks.

Computer simulations are also beginning to shed light on the fusion of bilayer membranes — a topological transformation that is crucial for intracellular transport and communication. In this process, one starts from two separate nano- or microcompartments simulating two unilamellar vesicles. These compartments adhere to each other, and the adjacent bilayers within the adhesion zone then undergo molecular reorganization leading to the formation of a fusion pore: a smooth neck-like connection between the two bilayers. However, in spite of a lot of experimental work, both on biological and on biomimetic membranes, some basic properties of membrane fusion are still unknown. One such property is the timescale for the formation of the fusion pore. So far, the most sensitive experimental techniques applied to this formation process are patch clamp methods from which one concludes that the fusion pore is formed within less than 100 μs (ref. 8). In contrast, recent computer simulations of coarse-grain models indicate that this process is much faster and can be completed in about 200 ns (J. Shillcock and R. Lipowsky, unpublished work). Thus, there is still a relatively large gap between the length and timescales that are accessible to computer simulations and experimental probes of membrane processes. This gap is shrinking, however, and will eventually vanish as we further develop both types of research tools.

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MATERIAL WITNESS
A blast from the past

Sometimes you never know when a material will come into its own. Fifty years ago there was a small flurry of work on a rather obscure class of metal oxides, manganites with a perovskite structure. These materials had interesting magnetic properties: they exhibited a phenomenon dubbed double exchange, wherein electron spins on adjacent mixed-valence metal ions are coupled by delocalization of an electron between them.

This process, explained by Clarence Zener (of Zener diode fame) in 1951, posed a nice theoretical challenge, and it drew the attention of two future Nobel laureates (Philip Anderson and Pierre-Gilles de Gennes) as well as John Goodenough, now arguably the world's leading expert on the behaviour of metal oxides. But despite the calibre of the researchers, no one would have guessed that papers with titles like 'Interaction between *d*-shells in transition metals. II. Ferromagnetic compounds of manganese with perovskite structure.' were destined for great things.

Yet this, Zener's original paper on double exchange in manganites (*Physical Review* 82, 403–405; 1951), has just been ranked as the paper with the sixth highest impact among all the publications in the *Physical Review* (*PR*) journals since 1893. A publication on the subject by Anderson ranks at number 19, de Gennes' at 21, and Goodenough's at 37.

Even more remarkably, all four papers, along with one by E. O. Wollan and W. C. Koehler on neutron diffraction from manganites (published in 1955, ranked 37), made very little impact at the time of publication. They were cited just a few times a year, if at all, until the mid-1990s, when the citation statistics for all of them soared. In 2000, Zener's paper was cited over 100 times within the *PR* journals alone.

They were classic 'sleepers'. These papers suddenly became hot when it was discovered in 1993 that thin films of manganite materials exhibit so-called colossal magnetoresistance: their electrical resistance changes dramatically in the presence of a magnetic field. This is the crucial characteristic of readout heads for magnetic data storage, and the manganites were suddenly of vast technological interest.

This history of the early work on manganites emerges from a fascinating analysis by Sidney Redner of Boston University of the citation statistics of all the papers published in the *PR* journals since they began 111 years ago (xxx.arvix.org/abs/physics/0407137). The extraordinary burst of citations of the manganite studies, 40 years after their first appearance, is 'unique in the entire history of *PR* journals', Redner says.

Nonetheless, the significance of that work fits within the general consensus from Redner's list of highest-impact papers in *PR* journals, which is to say that twentieth-century physics was largely about condensed matter, and more specifically about the quantum-mechanical theory of electronic and magnetic properties in the solid state. The top two papers, both co-authored by future Nobel laureate Walter Kohn, established the density-functional theory by which means electronic band structures are typically calculated. The story Redner's study tells is one of physics' persistent engagement with materials and technology.

Philip Ball