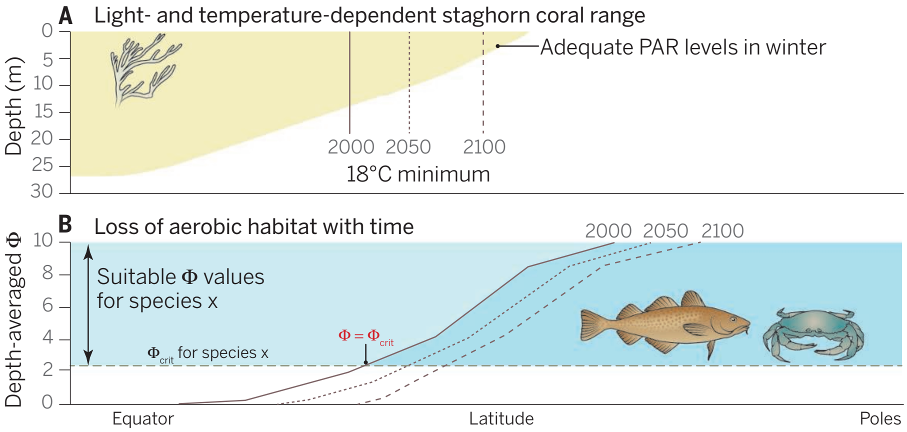

Invisible barriers. Muir *et al*. show that even though higher water temperatures will allow corals to colonize higher latitudes, low wintertime light levels will restrict them to progressively shallower depths (**A**). Furthermore, Deutsch *et al*. show how the depth-averaged metabolic index (Φ) for a given marine species decreases from higher latitudes to lower latitudes, often to levels that fall below the critical metabolic limit (Φ_{crit}) (**B**). With future increases in temperature and decreases in O_2 concentrations, the metabolic boundary of the species (where $\Phi = \Phi_{crit}$) is shifted poleward. Both panels are conceptual and should not be used to extract numerical values.

irradiance reaching the ocean surface and its attenuation with depth are not expected to change much with changes in climate. Reef-building corals, such as the staghorn corals studied by Muir *et al.*, depend on photosynthetic symbionts, limiting them to depths with sufficient levels of photosynthetically available radiation (PAR) throughout the year. Near the equator, this depth is typically around 25 to 30 m. Outside the tropics, it shallows by about 0.6 m per degree latitude, and so do the depths at which these corals are found. Muir *et al.* show that as reef-building corals settle at higher and higher latitudes in response to warming temperatures (*6*–*10*), they will eventually be confined to waters too shallow to support growth. Low PAR also appears to similarly limit the poleward expansions of other benthic photosynthesizers (*11*).

Other barriers to range extensions are dynamic (see the figure, panel B). Although rising temperature can lower barriers to poleward dispersal, such as minimum temperature limits, it also raises others. Warmer waters hold less oxygen, and warming at the ocean surface increases stratification, which leads to less oxygen at depth. At the same time, the metabolic oxygen demand of organisms increases with rising temperature. Using physiological data for various fish and invertebrate species, Deutsch *et al.* apply an energetics approach to determine how these changes affect the habitable space of several marine species. They define a metabolic index Φ, which is the ratio of O_2 supply and metabolic O_2 demand, and thus captures the minimal physiological requirements for survival. Φ_{crit} is the sum of Φ and the additional energy required for key ecological activities. For the species studied, Φ_{crit} ranged from 2 to 5, suggesting that species are limited to environments where they can sustain metabolic rates that are 2 to 5 times their resting rates. These values are quite close to those for terrestrial organisms and may thus reflect basic metabolic requirements of organisms. Deutsch *et al.* find that if climate change proceeds along its current path, the habitats for the species they studied will contract by ~20% by the end of this century.

Both studies highlight little-recognized barriers to future range expansions in the oceans. Each is based on physiological limitations of marine organisms that are quantifiable and thus increase our ability to predict species habitats into the future. More difficult to quantify are the consequences of climate change on species interactions, which will reshape marine communities and the ranges of their species in complex nonlinear ways (*12*). Thus, although studies such as Muir *et al.* and Deutsch *et al.* increase scientists' confidence to pencil in the lines around future species distributions, we still need to keep the erasers handy. ■

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FRICTION

Slippery when dry

Stiff nanodiamond particles encapsulated in graphene can substantially reduce friction for water-free macroscopic surfaces

By **James Hone**[1] *and* **Robert W. Carpick**[2]

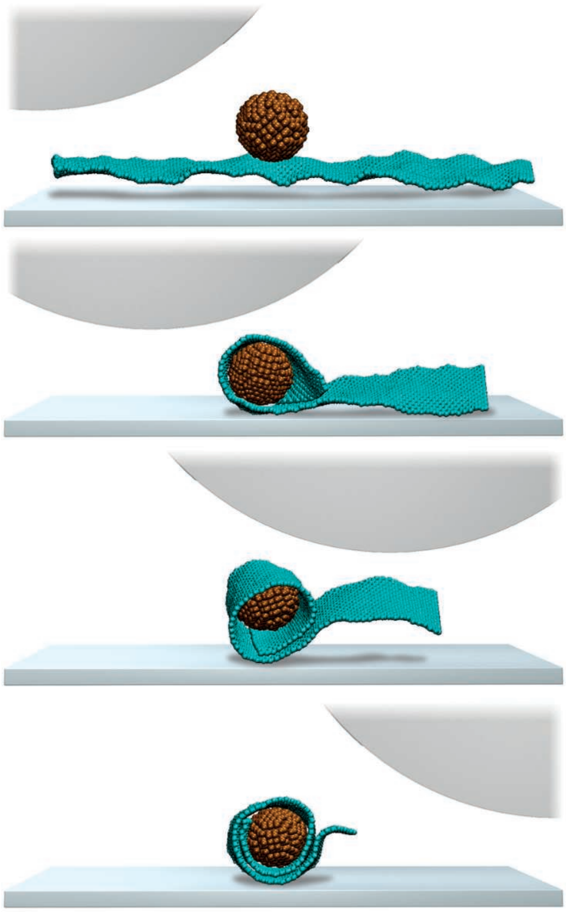
Friction and wear account for massive amounts of wasted energy annually (estimates run in the hundreds of billions of dollars in the United States), in addition to unwanted and even unsafe failures of vehicles, machines, and devices (*1*). For example, nearly one-third of a vehicle's fuel energy is spent on overcoming engine, transmission, and tire friction (*2*). Engineers have devised many ways to reduce and control friction and wear, but it remains unknown whether superlubricity—the reduction of friction forces to nearly immeasurable levels—can be achieved with practical materials. On page 1118 of this issue, Berman *et al.* (*3*) describe an approach that combines the advantages of two nanomaterials with very different mechanical properties—stiff nanodiamonds and bendable graphene—to achieve apparent superlubricity on the macroscopic scale.

Superlubricity has been observed for a range of materials including practical amorphous diamondlike carbon (DLC) coatings (*4*). However, most reports describe very well-controlled nanoscale contacts or specific experimental conditions (e.g., ultrasmooth surfaces) for limited durations with coatings that must be applied with advanced thin-film deposition methods. Graphene's distinctive properties make it a promising material in the search for practical superlubricity. It is extremely rigid in-plane and is not likely to form bonds with other materials it contacts, which suggests that it should shear across itself (or other materials) with ease. Indeed, graphite flakes work as a lubricant for this primary reason, and isolated domains of single graphene on substrates have been shown to exhibit order-of-magnitude reductions in friction relative to the surrounding substrate (*5*).

Graphene's surface is crystalline, which allows it to achieve a condition known as "structural lubricity," a type of superlubricity in which surfaces with different atomic lattices are incommensurate, like egg cartons for different-sized eggs. The potential energy between the two surfaces is almost completely independent of position, so that the two surfaces never lock together and slide easily. Previous investigations, first in nanoscale contacts (*6*) and more recently on the scale of 1 µm (*7*), showed that superlubricity can exist between misaligned graphitic surfaces. In addition, concentric carbon nanotubes, in which the inner and outer shells are by nature incommensurate, have been shown to exhibit ultralow friction arising from structural lubricity up to lengths of centimeters (*8*).

Large-area graphene sheets (grown by chemical vapor deposition) and liquid suspensions of micrometer-scale graphene flakes have both been investigated for their potential as tribological coatings. However, initial studies have so far not shown great promise, likely because single-layer graphene weakly adheres to surfaces and easily delaminates (*9*, *10*). Recently, graphene flakes deposited in suspension on steel were shown to be durable across a range of environments, but the friction coefficient of ~0.15 to 0.2 was not as low as can be achieved with graphite. Another complication is that the low friction seen for few-layer graphene at the nanoscale deformation actually goes up, by nearly 50%, as the number of layers reduces to one, because the thinner the sheet, the greater its ability to flex and wrap around an asperity to increase contact area and friction (*11*).

Motivated by the potential for superlubricity between the incommensurate lattices of DLC and graphene, Berman *et al.* explored the frictional properties of SiO_2 coated with graphene flakes deposited from liquid suspension, against a large (1 cm) steel ball coated with DLC. However, the friction coefficient was well above the regime of superlubricity. In examining the wear tracks from these experiments, they observed that the graphene had delaminated from the surface and rolled up into "nanoscrolls," similar to previously observed fullerene "onions" and consistent with the ease with which graphene, given its thinness, can flex, bend, and roll up.



Squeeze wrap. Berman *et al*. found that huge reductions in macroscopic friction ("superlubricity") were achieved where nanodiamonds slid against graphene. The nanodiamonds bonded to graphene nanoplatelets and became wrapped in them, allowing them to slide easily through incommensurate surface effects.

Berman *et al.* recognized that such nanoscrolls might in themselves be quite useful as an antifriction coating if it were not for their easy deformability under pressure. Thus, they added nanodiamond particles, 3 to 5 nm in diameter, to the graphene suspension as a way to mechanically stabilize the nanoscrolls. The frictional coefficient was initially similar to that achieved with graphene only, but upon repeated cycling, the coefficient of friction dramatically decreased to 0.004. This reduction was not observed with either the graphene or nanodiamond alone, and was also only seen in a dry environment—the friction coefficient was nearly 100 times greater in high humidity.

Investigations by Raman spectroscopy, transmission electron microscopy, and detailed molecular dynamics simulations enabled Berman *et al.* to describe the process by which superlubricity is achieved. First, sliding of the nanodiamonds across the graphene platelets induces bonding between the graphene nanoplatelets and the diamond (see the figure). This process is facilitated both by the dangling bonds on the diamond surface and defects in the solution-produced graphene, such as those at the edges of the isolated graphene particles. The graphene then rolls around the diamond to make spheres ~10 nm in diameter. These spheres are nearly rigid, providing mechanical stability. Furthermore, the ordered surface provides an incommensurate atomic contact with the DLC-coated sphere, leading to superlubricity from the structural mismatch.

Unfortunately, water interrupts this rolling process by increasing adhesion of the graphene to the surface and by stabilizing defective sites in the graphene that provide bonding to the nanodiamond. Still, achieving such low friction for sustained times under macroscopic conditions, where roughness, irregularities, and high local stresses at nanoscale contact points could easily trigger failure of such thin coatings, is surprising and promising. Moreover, the solution-based deposition methods are relatively simple. Taken together, these findings suggest that practical coatings that take advantage of graphene's remarkable properties may be practically attainable.

Although more work is needed to fully verify the hypotheses behind the remarkable observations, the results of Berman *et al.* are intriguing for many reasons. Other combinations of two-dimensional materials (such as molybdenum disulfide) with other types of nanoparticles may prove more tolerant of water, or could open up their use as additives in lubricant fluids to reduce the large and undesirable amount of friction in vehicles. The potential for reduced energy consumption renders the result important in itself, and worthy of inspiring further studies that build upon it. ■

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Slippery when dry

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