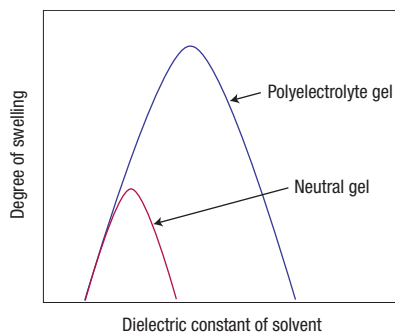


with  $\epsilon = 8.9$ ) than that of the neutral polymer, as shown schematically in Fig. 2. This suggests that, in contrast to the neutral gel, the paired ions in the polyelectrolyte gel raise the dielectric constant of the polymer, allowing swelling with more polar solvents. Once enough swelling occurs, some of the counterions dissociate, causing the increased swelling observed for polyelectrolyte gels compared with neutral ones<sup>3</sup>.

A notable exception to the general picture described above is the solvent ethyl acetate, which does not swell either the neutral or polyelectrolyte gel at all, even though ethyl acetate has a dielectric constant of 6. Clearly, ethyl acetate has an unfavourable interaction with the polymer chain used to make these gels. Presumably another requirement for swelling polyelectrolyte gels is that the solvent must solvate the counterions, and ethyl acetate is known to not solvate ions and instead promotes the association of ions with each other<sup>6</sup>.

A very interesting question is whether such gels could be used for



**Figure 2** Relative swelling degrees of neutral and polyelectrolyte gels.

separations. As tetrahydrofuran (THF;  $\epsilon = 7.5$ ) swells the gel greatly whereas dimethylformamide (DMF;  $\epsilon = 38$ ) does not, could these polyelectrolyte gels extract THF from a DMF/THF mixture? The entropy increase associated with mixing the counterions within the gel with solvent would have to work

in opposition to the loss of entropy associated with the two solvents being separated.

In terms of applications, the most desirable possibility would be to find a gel that could absorb many times its mass of hydrocarbon oils to clean up oil spills that profoundly impact the environment<sup>7</sup>. Unfortunately, based on the fact that the maximum swelling of even these polyelectrolyte gels strongly decreases with decreasing dielectric constant of the solvent, the ability of a gel to absorb a solvent like a hydrocarbon oil, with  $\epsilon = 2$ , is doubtful.

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## MATERIAL WITNESS

### Feel the force



It was arguably high-temperature superconductivity that first made physicists realize how materials can be regarded as another 'variable' to be tweaked in the lab so that new aspects of physical phenomena can be probed. Of course,

the history of using new materials to investigate new physics is older, perhaps beginning in earnest with the inception of semiconductor technology; but this was often characterized by a sense that one must take what one is given, or that at best a change of material offers minor variations on a theme.

The development of the new superconductors, though often hit-and-miss, showed that the nature of the material could be qualitatively bound up with the physics. With the advent of optical metamaterials, this notion has now been fully turned around: the physics, if you like, is put in by hand through materials design to enable things that elude nature.

The principle of using materials as a free parameter much like temperature or

pressure is evident in recent proposals by Federico Capasso of Harvard University and his co-workers to engineer the Casimir force (F. Capasso *et al.* *IEEE J. Select. Topics Quant. Electr.* **13**, 400–414; 2007). This force between two objects separated by a very small gap arises from quantum zero-point fluctuations of the electromagnetic field between them: it is a kind of pressure due to the suppression of some fluctuation wavelengths in the intervening space.

Traditionally physicists have tended to regard the Casimir force as another 'given', a function merely of the geometry of the two interacting objects. The case of two metal plates first analysed by Hendrik Casimir in 1948 was later generalized by Evgeny Lifshitz to dielectrics, but that was about as far as it went in terms of recognizing a materials-dependent influence.

Although the Casimir force is basically the same phenomenon as the van der Waals attraction — crudely, it is what the latter becomes at larger separations — it is difficult to measure, because the interaction becomes strong only for rather large surfaces separated by small distances. Decisive high-precision

measurements weren't made until 1997, and much recent work has focused simply on characterizing the force for real metals.

But the advent of engineering at the micro- and nanoscales has awakened interest in the consequences of the Casimir effect, both positive and negative, for devices such as microelectromechanical systems. Although this raises the notion of tuning the force to advantage, surprisingly little attention has been given to how the nature of the material might be exploited.

Capasso and colleagues show, for example, that a suitably chosen sandwich of layers should generate a repulsive rather than an attractive force, enabling 'Casimir levitation'. And materials with anisotropic optical properties (birefringence) would produce a force that varies with the angle between the optical axes, creating a torque. Capasso also suspects that an effect on the force should be felt when the materials undergo phase transitions, for example from metal to insulator or superconductor. All of this is largely unexplored territory, and promises rich pickings.

**Philip Ball**