of the digital approach hinges on the key observation that the effective permittivity of the two-dimensional bytes can be largely controlled by adjusting the volume fraction of the respective material components or their relative ordering. In particular, when metals (such as silver) and insulators (such as silica) are mixed together, bytes can assume values that are vastly outside the range supported by the individual materials bits. Following this strategy, Della Giovampaola and Engheta discuss detailed digital designs for a number of metamaterial elements such as flat optical lenses and hyperlenses[9,11] that overcome the fundamental limit to image resolution and produce magnified images of objects smaller than the wavelength of the imaging light. Digital constructs for metamaterials with permittivity attaining near-zero values, or epsilon-near-zero materials[12], are also provided, amply demonstrating the versatility of the proposed approach.

Designing nanoscale bytes that exhibit a large range of permittivity values using the same two material bits mixed in different proportions is a powerful step having far-reaching consequences. It unlocks a simple route to the digital synthesis of artificial materials that can perform complex and specialized optical functions. For instance, similar to the discretization of an arbitrary analog signal achieved by simple binary algebra, it becomes possible to tackle the all-important optical inversion problem by direct 'digitization' of desired optical parameters using locally approximating metamaterial bytes.

Building on these powerful notions, it is conceivable that in the near future digital metamaterials could significantly advance a number of research fields, such as integrated optics and photonics, which rely on the manipulation of electromagnetic fields by designed optical media in various wave-based devices and systems. The digital metamaterials vision could also significantly simplify the design of deterministic non-periodic optical media, which is a promising path to controlling wave localization, photon transport phenomena and optical confinement over broad spatial, angular and frequency spectra[13]. Moreover, the digital metamaterials concept could guide the synthesis of light-emitting and light-absorbing devices such as miniaturized lasers and solar cells with more efficient light–matter interaction. The same approach could also boost the efficiency of nonlinear optical phenomena, such as second- and third-harmonic generation beyond what is currently achievable with natural materials. Optical information storage and processing at the nanoscale could then be enabled by further advancements in digital metamaterials.

However, to fully exploit the potential of the proposed digital synthesis of optical materials, several challenges remain to be addressed in future investigations. Suitable material bits need to be carefully selected to eliminate, or at least strongly reduce, the optical losses that are intrinsic to the metallic components of large-scale digital metamaterials. Furthermore, future studies should focus on developing experimental strategies for the synthesis and nanofabrication of such digital metamaterials. The high level of nanoscale resolution and uniformity across large areas required to fabricate both two- and three-dimensional digital metamaterials seems difficult to achieve using currently available tools, necessitating further investigations and novel approaches. Finally, it is also expected that fundamental questions related to the attainable wavelength bandwidth of digital metamaterials will soon be addressed, potentially resulting in a fundamental understanding of the factors that govern broadband operation and nonlinearity in digital media.

All communication is essentially digital, was Shannon's major precept. Will this principle extend to the synthesis of metamaterials and innovative optical devices in the future? The study of Della Giovampaola and Engheta is certainly a pioneering first step in this direction. ❐

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NANOPHOTONICS

Hyperbolic phonon–polaritons

Hexagonal boron nitride nanostructures are shown to sustain phonon–polariton modes with comparable performances to plasmon–polariton modes in graphene but with lower losses.

Zubin Jacob

Polaritons, collective excitations that originate from the coupling of photons with matter, are uniquely poised to stimulate the generation of applications beyond the reach of conventional electronics and photonics. From exciton–polaritons combining semiconductor electron–hole pairs with light for low threshold lasing[1] to plasmon–polaritons mixing free-electrons and photons for nanoconfinement of electromagnetic fields[2] on metals, unique applications are being developed for all kinds of polaritons. Thus the recent discovery of strongly confined phonon–polariton modes in hexagonal boron nitride (hBN) could result in new imaging, thermal and quantum applications in the mid-infrared (mid-IR) wavelength region[3–5].

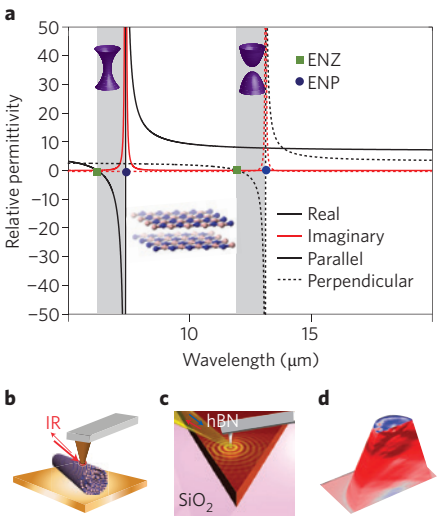

Figure 1 | hBN phonon–polariton properties. **a**, Relative permittivity of hBN (bottom inset) showing the existence of two Reststrahlen bands (shaded grey regions) and corresponding epsilon-near-zero (ENZ) and epsilon-near-pole (ENP) wavelengths. The anisotropy of the relative permittivity gives rise to hyperbolic isofrequency surfaces (top insets) and strongly confined bulk polaritons in this spectral range. **b**–**d**, Recent experiments have demonstrated the existence of 1D (**b**; ref. 4), 2D (**c**; ref. 3) and 3D (**d**; ref. 5) phonon–polaritons with ultrahigh refractive index values in hBN at the nanoscale. IR, infrared. Figures reproduced with permission from: **b**, ref. 4, 2014 Nature Publishing Group; **c**, ref. 3, © 2014 American Association for the Advancement of Science; **d**, ref. 5, 2014 Nature Publishing Group.

Phonon–polaritons are collective oscillations (or modes) resulting from the coupling of photons with optical phonons (that is, quanta of lattice vibrations) in polar dielectrics. The characteristic frequencies at which these modes occur fall in the mid-IR wavelength range for most materials. At the phonon–polariton resonances, the dielectric permittivities of such materials assume unique forms, either passing through a zero ($\varepsilon \approx 0$) or being enhanced to large values at a pole ($\varepsilon >> 1$; Fig. 1). In between the epsilon-near-zero (ω_{LO}) and epsilon-near-pole (ω_{TO}) frequencies (Fig. 1), these media behave like a conventional metal and strongly reflect incident radiation. This range of frequencies, for which light propagation is forbidden, is called the Reststrahlen band.

Recent works published in *Science*[3] and *Nature Communications*[4,5] have shed light on fundamental phenomena taking place within this forbidden band for a very unique phonon–polaritonic medium: hBN. The weak van der Waals bonded nature of this material makes it optically anisotropic, meaning that the dielectric responses in perpendicular crystallographic directions (in-plane and out-of-plane) have opposite signs. This makes hBN a natural hyperbolic material[6,7]. The hyperbolic polaritons produced within bulk hBN allow electromagnetic modes with large momenta to propagate within the otherwise forbidden Reststrahlen band.

Writing in *Science* Dimitri Basov and co-authors[3] have shown that thin layers of hBN sustain phonon–polaritons that possess very similar properties to those of graphene plasmons. A tapered two-dimensional (2D) hBN crystal was used to launch surface phonon–polariton (SPhP) waves, which interfered due to reflections from the crystal edges. Near-field measurements of the resulting standing waves revealed that the SPhP wavelengths were 25 times smaller than their free-space value and their propagation lengths were 10 times higher than those of graphene plasmons[8], due to their low losses (Table 1).

More recently, writing in *Nature Communications* Gilbert Walker and co-authors[4] report on one-dimensional multiwalled hBN nanotubes that support cylindrical phonon–polaritons at mid-IR wavelengths. The authors measure effective refractive indices as high as 70 using scattering-based scanning near-field optical microscopy and report tunability of the 1D phonon–polariton modes and of the propagation lengths through varying nanotube size and substrate roughness.

Also writing in *Nature Communications* Joshua Caldwell and co-authors[5] describe how hBN conical nanoscale resonators couple free-space photons to bulk hyperbolic phonon–polaritons. The large confinement of the electromagnetic modes is due to hyperbolic polaritons with large momenta, which form volumetric standing waves inside the conical hBN nanoscale resonators. The effective refractive index of these modes was measured to be as large as 86, with moderately low loss. This needs to be compared with, for instance, titania, one of the highest refractive index natural materials in the visible, which has a refractive index of 2.5.

Naturally occurring hBN shows epsilon-near-zero[9], epsilon-near-pole[10] as well as hyperbolic behaviour, which are all key aspects of hyperbolic metamaterials: man-engineered artificial photonic media with exotic optical response and hyperbolic dispersion. Hyperbolic metamaterials are one of the most interesting classes of metamaterials that possess unique bulk waves that can enhance spontaneous emission from light emitters as well as black-body thermal radiation[11]. These effects, if explored in hBN, a naturally occurring hyperbolic material, could have major implications due to the advantages given by the continuous nature of a natural medium, as opposed to the unit-cell limitations typical of artificial metamaterials[12]. Other important applications could be in sub-diffraction imaging[13] and sub-surface sensing[14] using hyperbolic polaritons in the mid-IR range, the spectral region where hBN SPhPs function.

This being said hBN might not be the answer to all troubles. Phonon–polaritons are notorious for their large dispersion and resonant characteristics. This means that, even if their losses are smaller than the ones experienced by their plasmon–polariton counterparts, their group velocity and their induced field-enhancement are fundamentally diminished by their large dispersion. In the future it will be interesting to see which class of polaritons will hold the key for low loss as well as low dispersion propagation, mimicking photons in glass, while simultaneously providing sub-diffraction confinement. ❐

Table 1 | Table of loss constants (Γ) comparing media sustaining plasmon–polaritons and phonon–polaritons in the mid-IR spectral range.

Material	Type	Γ (meV)
InGaAs (doped semiconductor)	Plasmonic	6.59
Graphene	Plasmonic	4.87
SiO_2	Phononic	3.85
SiC	Phononic	0.65
hBN (*c* axis)	Phononic	0.87
hBN (*ab* axis)	Phononic	0.25

Values taken from refs 1–14.

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MATERIAL WITNESS

THE FORCE OF SHAPE

PHILIP BALL

Entropic forces feature throughout condensed-matter science. The depletion force has its origins in solution chemistry, and is generally considered to be an entropic effect of the steric exclusion of solutes close to and between surfaces[1] — although deducing the relative importance of entropic effects in real systems that also exhibit enthalpic effects is not trivial[2]. Helfich's seminal work on membrane fluctuations[3] revealed that their suppression in adjacent membranes can induce an entropic repulsion — although here too the details remain unclear[4]. The entropic consequences of confinement also supply one way of understanding the critical Casimir force between surfaces that confine fluid mixtures[5]. The hydrophobic interaction, central to biophysics, has been given an entropic interpretation[6], although there's debate over the details[7,8].

The crystallization of colloidal hard spheres is also considered to be an entropically driven phase transition[9]. Here the hexagonal crystal structure observed experimentally is a simple consequence of close-packing requirements. But if the particles are non-spherical, the optimal packing geometry is not always clear. Damasceno *et al.* have recently shown that arbitrarily shaped hard polyhedra display considerable predictability in their dense packing arrangements, but that the influences on these structures are subtle and the outcomes diverse[10]. Depending on their shape, some polyhedra will form ordered crystals, while others form liquid crystals, 'plastic' crystals in which the particles rotate freely, or disordered glasses. The entropic forces promoting the dense phases here heed details of particle shape: in particular, there is often a propensity for particles to sit face to face with facets aligned, creating directional preferences that can lead to ordered self-assembly.

These processes of non-spherical particle packing are relevant to the crystallization of viruses, many of which are faceted polyhedra, and also of proteins, the shapes of which are less geometric but often strongly anisotropic. For synthetic nanoparticles an increasing ability to control shape permits the exploration of diverse packing phenomena[11], while the use of DNA to make complex molecular polyhedra adds a new dimension bridging the biological and the nanotechnological[12]. There is good reason, then, to seek a clear grasp of how shape exerts an entropic influence.

This is what van Anders *et al.* now provide[13]. Using computer simulations of polyhedral packings, they clarify the concept of a shape-dependent directional entropic force, showing that it can be given a rigorous description based on the role of shape and faceting in maximizing the entropy of dense packings. As such, the force is an emergent property of local particle configurations, and it typically manifests itself for polyhedra as a repulsion between corners and an attraction between faces. For these systems the force is typically of the order of a few kT (where k is Boltzmann's constant and T is temperature), making it comparable to van der Waals and depletion forces. It should, the researchers say, be experimentally measurable.

The directional entropic force offers a way to distinguish simple packing, driven by global density considerations, from self-assembly that is sensitive to local geometry. It helps rationalize why a self-assembled system doesn't necessarily seek the densest packing, and offers a tool for designing such assembly processes. ❐

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