Negative refraction

Negative refraction is one of the most fundamental phenomena in nature. It gives rise to such well-known effects as the apparent bending of objects partly immersed in water, rainbows, mirages, green flashes, and haloes. Refraction is also utilized in many existing optical instruments, including microscopes, telescopes, and eyeglasses. All these phenomena and applications rely on conventional or “positive” refraction. What would the world look like if the sign of refraction were reversed?

The law of refraction predicts that an electromagnetic wave, crossing the interface between two materials with refractive indices \( n_1 \) and \( n_2 \), changes its trajectory, depending on the difference in the refractive indices, such that \( n_1 \sin \theta_1 = n_2 \sin \theta_2 \) where \( \theta_1 \) and \( \theta_2 \) are the angles from the normal of the incident and refracted waves. The direction of the refracted wave depends on the sign of \( n_1 \) (assuming \( n_1 > 0 \)).

The refraction is referred to as positive when \( n_1 > 0 \) (Fig. 1a) and as negative when \( n_1 < 0 \) (Fig. 1b). While positive refraction is a well-known phenomenon, a negative index of refraction leads to many unusual and often surprising effects. For example, Fig. 1c and d show calculated images of a metal rod in a glass filled with regular water and in a glass filled with negative-index water.

Left-handed world. The refractive index is one of the basic characteristics of electromagnetic wave propagation in continuous media. It is closely related

![Fig. 1. Refraction: Diagrams of (a) positive refraction and (b) negative refraction, and calculated images of a metal rod (c) in a glass filled with regular water \( n = 1.3 \), and (d) in a glass filled with “negative-index water” \( n = -1.3 \).](image-url)
to two fundamental physical parameters that characterize material properties, the dielectric permittivity \( \varepsilon \) and the magnetic permeability \( \mu \), through the equation \( n = \sqrt{\varepsilon \mu} \). While nearly all transparent conventional materials have positive \( \varepsilon \) and \( \mu \), corresponding to positive \( n \), there are no fundamental physical reasons prohibiting materials from possessing simultaneously negative \( \varepsilon \) and \( \mu \), and as a result negative \( n \). Although not found in nature, such materials were recently created artificially and were named “meta-materials.”

A detailed theoretical study of electromagnetic wave propagation in materials with simultaneously negative \( \varepsilon \) and \( \mu \) was performed by Victor Veselago in 1967. Maxwell’s equations, which relate the electric field \( E \), the magnetic field \( H \), and the wave vector \( k \), predict that \( E, H, \) and \( k \) form a “left-handed” set and the sign of the refractive index is negative if both \( \varepsilon \) and \( \mu \) are negative, and a “right-handed” set if both \( \varepsilon \) and \( \mu \) are positive. The former class of materials is commonly referred to as left-handed materials or negative-index materials (NIMs), while the latter class is referred to as right-handed materials or positive-index materials (PIMs). At the same time, the direction of the Poynting vector \( S \), which defines the direction of the energy flow, is the same in positive-index and negative-index materials. Thus, the Poynting vector is antiparallel to the \( k \)-vector in negative-index materials and is parallel to the \( k \)-vector in positive-index materials. The opposite directionality of the \( k \)-vector and the Poynting vector is often taken as the most general definition of negative-index materials. Therefore, the negative refraction illustrated in Fig. 1 is a direct result of the opposite directionality of \( k \) and \( S \) and of the continuity of the tangential components of the wave vector at the interface between the two media.

Although the term “left-handed materials” was originally coined to describe materials with simultaneously negative \( \varepsilon \), \( \mu \), and \( n \), currently it is used in a broader context to include other optical structures that possess antiparallel \( k \)-vectors and Poynting vectors and support negative refraction. Examples of such materials include photonic crystals, anisotropic waveguides, organic and uniaxial gyrotropic crystals and a thin film on a metal substrate, and nanotransmission lines.

Negative refraction has been demonstrated at microwave frequencies in a metamaterial wedge and in the visible frequency range at the interface between a bimetallic AuSi/Ag waveguide and a conventional AgSi/ErAg slot waveguide using plasmons. Negative refraction at optical frequencies was demonstrated in photonic crystals. Although many unusual phenomena associated with the negative index of refraction can be observed in photonic crystals, the main limitation of photonic crystals is that the size of their characteristic features is comparable to the wavelength of light. On the contrary, optical metamaterials with feature sizes much smaller than the wavelength of light are predicted to enable many truly remarkable phenomena. However, currently optical metamaterials are available only in the form of subwavelength thin films, thus permitting the measurement of a phase advance but not of negative refraction per se.

Besides negative refraction, negative-index materials have been predicted to give rise to a wide variety of extraordinary linear and nonlinear optical phenomena, including reversed Cerenkov radiation, the reversed Doppler effect, backward phase-matched second-harmonic generation and optical parametric amplification, lasing without a cavity, bistability, and gap solitons in PIM-NIM couplers with no external feedback.

**Superresolution:** from “super” to “hyper” lens. A very unusual property of negative-index materials gives rise to the possibility of imaging using a flat slab of negative-index material with \( n = -1 \) surrounded by a conventional medium with \( n = 1 \). Moreover, under the appropriate conditions, this slab not only focuses propagating field components but also recovers the evanescent field components, which decay exponentially with distance from the source (Fig. 2a), through the excitation of a plasmon resonance on the surfaces of the negative-index material. These evanescent field components, which are responsible for imaging of the high-frequency and correspondingly small-scale features of the object, cannot be restored by conventional lenses, inevitably limiting their resolution. Thus, at least in the ideal (lossless) case, an imaging system based on a slab of negative-index material, named a “superlens” by John B. Pendry, has the potential for significantly improving resolution in the image plane. Unfortunately, a superlensing effect is extremely sensitive to losses in the negative-index-material slab. While the superlens is likely to be useful in numerous near-field applications, including biomedical imaging and nanolithography, superresolution in the far field is challenging.

Recently, a promising solution, a hyperlens, was proposed independently by Nader Engheta and...
Evgenii Narimanov. Instead of reamplifying and refocusing the evanescent field components as Pendry’s superlens does, a hyperlens converts those evanescent waves into propagating waves (Fig. 2b). Once all the components are propagating waves, they can easily be imaged by a conventional lens (microscope) in the far field (Fig. 2c). The only remaining limitation of a hyperlens is that the object plane must be situated very close to the hyperlens surface.

Optical metamaterials. Many of the predicted extraordinary properties of negative-index materials would not have been possible without rapid progress in the design and fabrication of optical metamaterials. As mentioned above, no materials in nature possess negative $\varepsilon$ and $\mu$ in the same range of frequencies. While dielectric permittivity of some existing materials is negative at certain frequencies, no isotropic materials with negative $\mu$ are known. Moreover, magnetism is usually weak at optical frequencies so that $\mu \approx 1$.

On the contrary, metamaterials are built of artificial or “meta” atoms, which are resonant structures such as split-ring resonators and paired metal nanorods or nanostrips. The meta-atoms can be engineered and arranged such that their $\varepsilon$, $\mu$, and $n$ are positive, negative, or even zero at any selected frequency. The first optical metamaterials with a negative index of refraction have been demonstrated using paired nanorods, and independently by another group using paired dielectric voids in metal.

While these first experiments confirmed the possibility of the realization of a negative index of refraction at optical frequencies, the negative-index materials were realized only in the form of subwavelength films and possessed significant losses. Some essential requirements for practical negative-index-material designs include minimized losses or a large ratio of the real and imaginary parts of $n$, often taken as a figure of merit, a broad bandwidth over which both $\varepsilon$ and $\mu$ are negative, optimized impedance matching, and realization of three-dimensional negative-index materials.

Using a self-supporting fishnet structure consisting of rectangular dielectric voids in parallel metal films, a figure of merit of 3 has been demonstrated at a wavelength $\lambda = 1.4 \mu m$. This structure represents the current state-of-the-art for optical negative-index materials. Recently, the first three-layered negative-index material with a figure of merit of 2.5 at $\lambda = 1.41 \mu m$ was also reported.

Refractive index engineering. While one of the original motivations behind the development of metamaterials was the demonstration of negative-index materials, metamaterial technology has stimulated rapid progress in an entirely new and exciting branch of modern optics, transformation optics, which is based on the idea of mapping a coordinate transformation to a set of material parameters, $\varepsilon$ and $\mu$. Metamaterials allow precise control over these material parameters and, more generally, enable refractive index engineering. Such mapping turned out to be particularly useful for cloaking applications and facilitated the first experimental demonstration of cloaking of a copper cylinder at microwave frequencies. In that experiment the object was concealed by a cylindrical metamaterial cloak built using split-ring resonators. The coordinate transformation and a schematic of the first nonmagnetic cloak operating at optical frequencies, as proposed theoretically, are illustrated in Fig. 3a. Figure 3b shows the results of numerical simulations of cloaking of an ideal metallic cylinder. Currently, in both microwave and optical cloak designs, the effect has been achieved at only one frequency. Obviously, broadband cloaking would be desirable for most practical applications, and further research is therefore required.

Finally, cloaking is only one realization of the great potential of transformation optics in conjunction with metamaterials. Other promising applications include field concentrators and a variety of reflectionless devices. Metamaterials are bringing new degrees of freedom for designing structures with almost any desired optical properties, thus presenting enormous opportunities for a wide range of applications relying on refractive index engineering.

For background information see MAGNETISM; MAXWELL’S EQUATIONS; PREEMPTIVITY; PLASMON; POINTE’S VECTOR; REFRACTION OF WAVES in the McGraw-Hill Encyclopedia of Science & Technology.

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New coatings for wood

There has never been a broader array of coatings for wood available on the market than now. In the past, coatings for wood, such as stains, primers, and top coats, were primarily oil-based. However, as new air-quality regulations have mandated lower volatile organic content (VOC) in architectural coatings throughout the United States and now proposed in Canada, manufacturers have had to reformulate their products to meet the new regulations. [Volatile organic compounds are organic chemicals that produce vapors readily at room temperature and normal atmospheric pressure, including gasoline and solvents such as toluene, xylene, and tetrachloroethylene, which form photochemical oxidants (including ground-level ozone) that affect health, damage materials, and cause crop and forest losses; many are also hazardous air pollutants.]

There are two primary approaches to reformulating a low-VOC coating for wood. In the majority of these reformulations, the solvent portion of the product has been replaced with water. In a smaller percentage of these reformulations, the amount of solid ingredients has increased significantly to produce a high-solids coating. Given the special characteristics of wood, each of these approaches has presented challenges to the coatings formulator and, ultimately, the user of these coatings.

Characteristics of wood. Wood is one of the world’s most common materials of construction. As such, it is a renewable resource, easy to use, and durable for centuries when properly maintained. It can come from hardwood, softwood, or tropical wood species. However, regardless of origin, once the tree is harvested, it is subject to swelling and shrinking as it gets wet and dries. Continued wet/dry cycles create a continuous movement of wood that causes stress between the wet surface and the dry interior. This stress causes cracking, warping, bowing, twisting, and cupping of wood, resulting in structural problems. This excessive moisture also invades microorganisms such as mold and mildew to grow, causing aesthetic problems. Continued exposure to moisture will lead to rot and destruction of the wood itself.

Thus, understanding the characteristics of wood is critically important for the coatings formulator. The very nature of wood’s reaction to water is what makes an oil-based coating an easier product to use on wood and a water-based coating more difficult to use on wood. When water-based coatings are applied to wood, they will usually swell the grain of the wood, causing grain raising (Fig. 1). This usually results in the need for sanding, especially on fine furniture and cabinetry. Because they tend to dry faster as the water soaks into the wood, water-based stains are subject to lapping, which is seen as a darker area at the overlap of two brush strokes applied side by side. Other problems can occur in exterior water-based coatings for wood such as poor water resistance and adhesion failure compared to oil-based coatings. In order to understand why these problems occur, it is necessary to know the basics of how water-based coatings are formulated and how they differ from their oil-based counterparts.

Conventional oil-based coatings. Conventional oil-based coatings usually have several basic categories of ingredients that can be broken down into four main groups: solvent, binder, pigments/fillers, and driers/additives. The solvent acts as a carrier for the other ingredients and usually comprises one or more petroleum distillates such as mineral spirits, mineral oil, or xylene. It is this component of oil-based coatings that contributes to the depletion of the atmospheric ozone layer, and its content is now regulated by governmental agencies.

Binders can be as simple as drying oils such as linseed, tung, teak, or soybean oil or more highly formulated chemicals such as alkyds (a class of adhesive resins made from unsaturated acids and glycerol), polyurethane, epoxies, silicates, and fluorinated polymers. These generally deliver the bulk of the protection properties to the wood. Binders can be used by themselves or in combination.

Pigments and fillers impart color and opacity to a coating. Pigments generally are composed of iron oxides that result in basic brown, red, and yellow tones, but they can be as sophisticated as highly formulated organic molecules that impart stronger, intense colors like deep greens, reds, and blues. The most common white pigment is titanium dioxide. Fillers are usually made up of mined materials such as clay, calcium carbonate, mica, talc, or diatomaceous earth (yellow, white, or light-gray, siliceous, porous deposit made of the opaline shells of diatoms). They

Fig. 1. Mixed grain patterns cause differences within wood that result in cupping and warping. Where the wood is cut from the tree determines how the wood will warp when exposed to water. (From Wood Handbook: Wood as an Engineering Material, USDA Forest Service)