space around the macromolecules, sometimes referred to as free volume, which leads to higher gas permeabilities. In 2005 (*2*), the first gas permeation data were reported for a new class of polymers called polymers of intrinsic microporosity (PIMs), which were not only more permeable than the vast majority of other polymers but also reasonably selective. This discovery, alongside others, has since prompted membrane technologists to reevaluate the upper bounds of performance that are achievable with polymeric membranes for a range of gas pairs (*3*). Subsequent developments of PIMs have led to fresh updates of the upper bounds for some gas pairs in 2015 (*4*) and separations involving carbon dioxide in 2019 (*5*).

The high free volume of a PIM arises from two features of the main chain of the polymer that discourages it from filling space (*6*). A PIM has, at least predominantly, a ladder structure with limited ability to change conformation. A PIM also incorporates units that force the backbone into a contorted shape. The first PIMs, prepared using aromatic nucleophilic substitution reactions, used spirocenters as "sites of contortion." Subsequently, other types of chemistry have been explored, and a variety of motifs, including what is known as Tröger's base and triptycene, have been used to create twisty polymer chains.

Recently, catalytic arene-norbornene annulation (CANAL) polymerization was introduced to generate contorted ladder polymers (*7*). In early examples, the contortions are essentially in two dimensions, leading to ribbon-like structures (*8*). Building on previous work, Lai *et al.* created dinorbornene monomers with an extra bend as the main ingredient for CANAL polymerizations alongside *p*-dibromo-*p*-xylene, which gave rise to three-dimensionally contorted polymers with high internal surface areas.

Chemical ingenuity enables polymers to be fashioned that trap free volume when formed into a membrane. But nature does all it can to squeeze out free volume over time, a process referred to as physical aging. Such aging usually leads to a reduction in gas permeability. However, this decrease in performance can be counteracted if the membrane can improve its selectivity as it physically ages. Thus, like a fine wine, the aging of a well-designed membrane can attain a better balance of properties over time. The three-dimensional (3D) CANAL polymer membranes prepared by Lai *et al.* show particularly good aging behavior such that over time, performances are achieved that surpass the state-of-the-art upper bounds for important gas separations such as hydrogen from methane. For example, over 158 days, the H_2-CH_4 selectivity for one of the CANAL polymers increased from just seven—allowing seven H_2 molecules to pass through for every CH_4 molecule—to an impressive 621.

Permeation studies often focus on single gases, with the selectivity for a pair of gases calculated simply as a ratio of the pure-gas permeabilities. This may not reflect what happens with a mixture of gases, where one gas can affect the transport of another, either because it competes for space within the polymer or because it influences the properties of the polymer itself. For example, in the separation of carbon dioxide from methane, the selectivities obtained with mixed gases are generally lower than those predicted from single-gas measurements. In 2008, a CO_2-CH_4 mixed-gas upper bound was established (*9*), based on data then available in the literature. This limit is surpassed by the aged 3D CANAL polymers of Lai *et al.* Mixed-gas selectivities of nearly 50 were achieved for one of the CANAL polymers after being aged at ambient temperature and pressure for 190 days, with another CANAL polymer offering even higher selectivities, albeit with lower permeabilities. The mixed-gas limit can also be surpassed for previous PIMs if the polymerization conditions are controlled to optimize the range of topologies present in the polymer, which may include looped, branched, and network structures (*10*).

PIMs that exhibit beneficial aging provide a route to enhanced membrane performance. This research brings closer the prospect of much more efficient polymeric membranes for hydrogen and carbon dioxide separations. However, the behavior of high free-volume polymers in films with thicknesses greater than 40 μm, as used in studies of material properties, does not necessarily translate into the performance of films less than 2 μm thick that are commonly found in commercial membranes (*11*). The next phase of research is to optimize and control the performance of these types of polymers in very thin films, as well as to extend the permeation studies to more complex, commercially relevant gas mixtures. ■

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QUANTUM GASES

Photons think inside the box

Light confined to a sheet offers a glimpse into low-dimensional quantum gases

By **Richard J. Fletcher**[1,2] *and* **Martin Zwierlein**[1,2]

When the light from distant stars streams across the Universe, it remains unperturbed by other light rays going about their own business. Despite their reluctance to interact with each other, photons are nevertheless particles, carrying energy and momentum just like molecules, atoms, and electrons do. This raises the possibility of creating exotic new types of matter, made not from those familiar massive particles but from light itself. On page 1403 of this issue, Busley *et al.* (*1*) report creating a quantum gas made from photons and confining it to a flat two-dimensional space. Just like a gas made from atoms, this photonic gas undergoes Bose-Einstein condensation (BEC) and adjusts its shape to that of its container.

"Busley *et al.* bring these advantages to quantum gases of light and explore a textbook scenario: a two-dimensional, spatially uniform gas of bosons."

Busley *et al.* use two closely spaced mirrors, between which photons reflect back and forth. Most of each photon's energy is devoted to its back-and-forth motion, leaving only a small amount of energy for its motion parallel to the mirrors. This restriction imbues each photon with an effective mass, meaning that it behaves like a conventional particle—albeit a very light one, with a mass only 10 millionths that of one electron. Crucially, in between the mirrors is a "dye," which contains molecules whose role is to continually absorb and emit photons. Because this dye is held at room temperature, the photon gas settles into thermodynamic equilibrium at a balmy 300 K.

In previous experiments that used this setup, the light was confined in the

transverse direction by using curved mirrors (*2*). This enforced an energy cost for the photons to move away from the center, trapping them like marbles rolling in a bowl. In comparison, Busley *et al.* use special mirrors that are flat aside from a square raised ridge, along which the gap between the two mirrors is reduced. From a photon's perspective, this results in a confining wall, creating a box inside which the photons are trapped. In the context of ultracold atomic quantum gases, in the past decade box traps have emerged as a powerful tool (*3*). This is because the confined gas in a box trap has a uniform density, meaning that one may probe its properties much more cleanly than in inhomogeneous systems. Busley *et al.* bring these advantages to quantum gases of light and explore a textbook scenario: a two-dimensional, spatially uniform gas of bosons (see the figure).

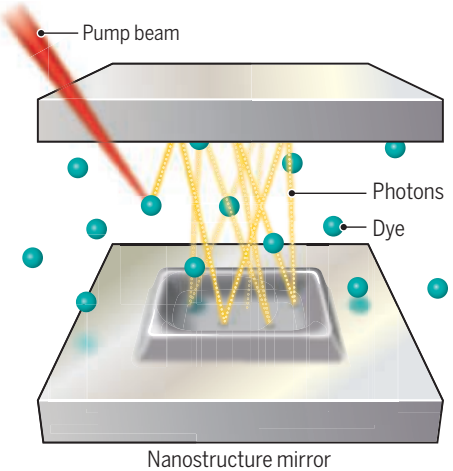
The physics of bosons in two dimensions has a fascinating history. In 1967, Pierre Hohenberg (*4*) showed that thermal excitations in two-dimensional quantum gases destroy long-range order at any nonzero temperature. This destruction of long-range order typically precludes BEC, which requires all the particles in a gas to share the same quantum state. Similarly, one may naively expect superfluidity, in which the gas flows without friction, to also be impossible. Superfluidity may nevertheless emerge in two-dimensional gases through the Berezinskii-Kosterlitz-Thouless (BKT) transition (*5*, *6*). This mechanism requires interactions between the particles, meaning that in the limit of vanishing interactions, the BKT transition occurs at absolute zero, which coincides with the temperature for BEC. This convergence of the BEC and BKT transitions was previously seen by using ultracold gases of atoms (*7*). However, experiments were not able to directly access the noninteracting regime because atomic gases rely on scattering between particles to mediate equilibration. By contrast, in the experiment by Busley *et al.* thermalization occurs indirectly through the dye, whereas the photons themselves do not interact with each other. This setup provides an almost perfect experimental realization of a noninteracting gas.

The question is which, if any, transition will occur in the two-dimensional photonic gas created by Busley *et al.*? The answer relies on two facts: The distance over which the particles' quantum states become scrambled grows as the temperature falls, and any real experimental system is finite in size. This means that upon cooling, eventually, the distance required for the quantum states to scramble exceeds the system size. This restores the possibility for all photons to share the same state and BEC to occur.

Busley *et al.* directly observe the formation of a BEC of light as the number of photons in the box is increased. At first, the photons occupy many different energy states, according to the same Maxwell-Boltzmann distribution that governs more "ordinary" gases, such as the air around us. However, when the total number of photons reaches a critical value, the population of the thermally excited states saturates, and additional photons start to pile up in macroscopic numbers in the quantum mechanical ground state. In previous work that used photons (*2*), BEC occurred because of the harmonic trap providing confinement (*8*). Here, a BEC is formed in the uniform box trap solely because of the presence of confining walls, whereas it would never occur in the case of an unconfined, infinitely extended gas.

Photons form a 2D quantum gas

Researchers have created a gas of photons confined to a two-dimensional space. A laser injects photons between two mirrors that restrict the photons' motion along the vertical direction but leave them free to explore the horizontal plane within the square wells. In between the mirrors, "dye" molecules continually absorb and emit the photons, which keeps the gas at a thermal equilibrium.



Given this newly created form of photonic matter, a natural question to ask is how it responds to applied forces. For example, can it be compressed? In contrast to an ordinary gas, a quantum degenerate gas should become more compressible as its density is increased. This unexpected effect occurs because as the gas approaches BEC, the population of higher-energy states saturates first. This means that any further added particles predominantly populate low-energy states. These only contribute weakly to the pressure of the gas, which therefore remains approximately constant despite the increasing gas density. Busley *et al.* measure the compressibility of their photon gas by tilting one of the confining mirrors, which caused the photons to accumulate on one side like water in a tilted bowl. Initially, as more photons are added, the gas becomes harder to compress. However, this behavior changes dramatically as the photonic gas becomes quantum degenerate, and the compressibility is seen to sharply increase. This effect is purely a consequence of quantum statistics and is cleanly demonstrated here by using noninteracting photons.

This work heralds the advent of quantum gases of light trapped in uniform box potentials. The ability to probe a homogeneous system at constant density is invaluable for studying its transport properties, excitations, and behavior near phase transitions. The experiments of Busley *et al.* reproduce several paradigmatic textbook results for a noninteracting but thermalized quantum gas in two dimensions—a regime that is difficult to explore otherwise. Looking ahead, the most interesting phases of matter arise once the constituents of a system begin interacting with each other, meaning that an important goal for future experiments is to persuade the trapped photons to react to the presence of their neighbors. In other systems, this has been achieved by allowing different photons to interact with cotrapped atoms (*9*, *10*). Alternatively, the authors suggest using a cavity medium whose properties presented to one photon are modified by the presence of a second. These developments in the ability to summon matter out of light offer exciting new perspectives, approaches, and surprises in the study of quantum gases. ■

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