moderate conductivity between chains when the backbone rings are aligned face-to-face, and very little conductivity between the widely spaced lamellar planes. High crystallinity optimizes the face-to-face alignment and so gives good conduction in a two-dimensional lamellar. However, the grain boundaries between crystallites limit conduction, and with a typical grain size on the order of 10 nm, there are plenty of disordered grain boundaries. The new polymers, designed to have a more rigid backbone, may have lower local crystallinity, but the polymer chains are aligned over longer distances (see the figure). Chabinyc and colleagues have mapped out the alignment and found that it extends for up to 1 μm (4, 5).

More conduction occurs along the favorable backbone direction, with less need for face-to-face conduction, and fewer large-angle grain boundaries to impede conduction. The long-range orientation of the rigid backbone polymers evidently more than compensates for the lower local crystallinity.

The disorder effects are also not simple. Noriega et al. point out that amorphous regions of the polymer have a larger band gap than the more ordered regions and should be excluded from the conduction process because carriers cannot reach them. Hence, a small crystallite surrounded by an amorphous grain boundary region creates a barrier impeding conduction to the next grain. Long-range orientation of the polymer allows the carriers to bypass the highly disordered regions without being affected and only move through the more ordered regions. The mechanism is analogous to the conduction of nanowire mats (6). Very-low-density mats of carbon or silver nanowires are highly conductive because their length allows them to intersect many other wires, and the empty spaces between wires do not impede the conduction. Such rodlike percolation may be a suitable model for the polymers. What matters is not whether the polymer is uniformly conducting, only that there are sufficient continuous conducting paths.

A mobility of 5 to 10 cm² V⁻¹ s⁻¹ has important technological consequences for flat-panel displays because it is the threshold needed by the TFTs that drives an organic light-emitting diode (OLED) display. The incumbent polycrystalline silicon technology has both cost and technological drawbacks that make it vulnerable to competition. It would be a nice vindication of organic semiconductor research if future displays have both organic TFTs and emitting diodes. However, there is tough competition from amorphous metal oxide TFTs (7) because their mobility of 10 to 20 cm² V⁻¹ s⁻¹ also puts them in the OLED range.

Their development raised a similar question of how an amorphous semiconductor can have such a high mobility. The explanation is that amorphous metal oxides have large s-orbitals that are spherically symmetric and insensitive to disorder in the bond angles, so that band tail states are few and shallow. The argument for the high-mobility polymers is also insensitivity to disorder but for a very different reason.

Single crystals of small conjugated organic molecules can have room-temperature mobilities up to 20 to 30 cm² V⁻¹ s⁻¹ (8), and theoretical calculations indicate that this value is about the upper limit for a polymer (9). It is not known how much closer a solution-deposited polymer can approach this limit. The gains in polymer mobility have come from trying new ideas for molecular designs, learning what works, and refining the design, and there is no reason to suppose that chemists will run out of ideas any time soon.

References

10.1126/science.1242935

PERSPECTIVES

Feedback on Galaxy Formation

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High-resolution radio images reveal how jets of relativistic particles can drive the dynamics of galaxy evolution.

The rate of star formation in galaxies peaked about 10 billion years ago when the universe was just over 3 billion years old. It has been in decline ever since. Whereas spiral galaxies, like the Milky Way, slowly churn disks of cold gas clouds into young blue stars, giant elliptical galaxies today are dormant. Despite having developed atmospheres of tenuous, 10-million-degree gas waiting to cool and form stars, the rate of star formation in galaxies (10) is very low, with the exception of the supermassive black holes coevolve with the galaxies (3) and perhaps even regulate their growth (3, 4, 7, 8).

How can a black hole with an event horizon smaller than the size of the solar system shape the structure of an entire galaxy? As matter falls into the growing black hole, its enormous gravitational energy is released in the forms of radiation and relativistic jets. The radiation and jets interact with the surrounding gas, driving it away from the black hole and out of the galaxy, thus preventing it from forming stars (7). This process, known as active galactic nucleus feedback, may be able to regulate the growth of the galaxy and the black hole itself (7, 8).

4C12.50 is an archetype in a class of burgeoning galaxies known as ultraluminous infrared galaxies (ULIRGs), the infrared luminosity exceeding 1 trillion times that of the Sun (9). Most of its infrared radiation is...
reprocessed ultraviolet light emitted by hot young stars and the accreting black hole. An ULIRG is enshrouded in cold (30 to 100 K) clouds and dust that are so thick that most of the ultraviolet light is unable to escape. Instead, it is absorbed by dust that then shines in infrared light. The cold molecular clouds and accompanying star formation in 4C12.50 are thought to have arrived in a catastrophic merger of two spiral galaxies. (The Milky Way’s star-formation rate is only a few solar masses per year, whereas star formation is proceeding at hundreds of solar masses per year in 4C12.50.) Most of the gas will be consumed by star formation. However, some will be expelled in winds driven by radiation pressure, supernova explosions (9), and by its powerful radio jets (1). Objects like 4C12.50 may eventually emerge as elliptical galaxies.

Relativistic radio jets are streams of plasma traveling near light speed, launched from the vicinity of supermassive black holes. Composed of charged particles and magnetic fields, they carry enormous energy and momentum flux. Their impact is clearly seen in x-ray images of elliptical galaxies and galaxy clusters. As radio jets push through the hot atmosphere surrounding the host galaxy, they inflate vast cavities that rise buoyantly (7). The bubbles and their associated shock fronts transfer the kinetic energy of the jet into the hot atmospheres, preventing them from cooling into cold molecular clouds. This process, in part, keeps elliptical galaxies from forming stars (7, 8, 10).

Apparently, this is only part of the picture. Morganti et al. show, using a clever technique, that radio jets interact not only with tenuous hot atmospheres, but also with cold, dense gas. The authors took advantage of situations where the synchrotron emission from the jet itself illuminates gas clouds from behind. The clouds then cast a radio shadow, a slight dimming of the radio flux, at a radio frequency that depends on the speed of the clouds along the line of sight. By combining signals from radio telescopes located around the world, the positions of the clouds can be pinpointed on the sky to a tiny fraction of an arc second. As long as the radio source is bright and the clouds are big enough and dense enough to absorb most of the radio flux striking them, they can be detected in galaxies at nearly any distance. Unfortunately, the technique is sensitive only to gas lying along the line of sight to the radio source. Therefore, the gas mass can only be estimated using the strength of the absorption feature. It cannot be measured directly.

Morganti et al. found cold clouds traveling toward us at about 1000 km s⁻¹ and at a rate of roughly 20 solar masses per year. The clouds will surely be driven away from the sites of star formation in 4C12.50 before they collapse into stars. Some may escape the galaxy entirely. Uncertainties in the outflowing mass make it difficult to determine the immediate impact on the star-formation history of 4C12.50 itself. Nevertheless, this result has broad consequences. It demonstrates that radio jets, which are common to all elliptical galaxies, can couple to dense gas and accelerate it to high speeds. Research using the new Atacama Large Millimeter Array is showing that radio bubbles can indeed drive outflows of molecular gas at rates of hundreds of solar masses per year. This process, known as radio-mechanical feedback, or radio mode feedback (10), was thought to operate only on the hot, tenuous atmospheres of galaxies and clusters. It now seems that radio mode feedback

Red and dead. Messier 87 is located 16 Mpc away in the Virgo cluster of galaxies. It is a nearby example of a “red and dead” giant elliptical galaxy harboring a (4 to 6) × 10⁹ M☉ nuclear black hole. Stars are in white, x-ray atmosphere is in blue, and radio synchrotron emission is in red. M87 is an archetypal example of a giant elliptical galaxy experiencing radio mode feedback (11).
operates on both the hot and cold gas in galaxies. Because of this and the fact that radio jets are a common and recurrent phenomenon in galaxies, radio mode feedback could be a key process that governs the growth of elliptical galaxies and the supermassive black holes lurking at their centers.

References

10.1126/science.1243114

ATMOSPHERIC SCIENCE

A Hyperventilating Biosphere

Inez Fung

In the Northern Hemisphere, CO₂ concentrations in the atmosphere oscillate regularly over the course of each year (see the figure). This “breathing” occurs because CO₂ declines in the atmosphere during the growing season, when CO₂ uptake via photosynthesis exceeds the release from microbial respiration, and increases during the rest of the year, when release exceeds uptake. On page 1085 of this issue, Graven et al. (1) present evidence that the breathing rate has accelerated greatly over the past 50 years.

The depth of the breathing is captured by the net ecosystem production (NEP), the integrated net uptake over the months when CO₂ uptake exceeds release (see the figure, panel A). NEP would equal the net release integrated over the rest of the year if the biosphere were at equilibrium, with growth balancing mortality and decay. NEP is greatest at high latitudes, where the growing season is short, and smallest in the tropics, where the monthly fluxes into and out of the atmosphere nearly cancel throughout the year.

Long-term increases in the amplitude of the annual CO₂ cycles were first noted by Pearman and Hyson in 1981 (2) and have since been established with increasing confidence. They have been attributed to increasing photosynthetic uptake, an earlier growing season, and increasing decomposition in response to changes in climate and atmospheric composition. Even so, the CO₂ monitoring stations are sparse and are located in remote marine locations, and it is not clear how widespread the biosphere response has been.

Graven et al., in a masterful stroke, have stitched together separate pieces of aircraft CO₂ records over the North Pacific (see the figure, panels B to D) to estimate the CO₂ amplitude trends in the middle troposphere, about 3 to 6 km above Earth’s surface. They find that the 50-year amplitude trends in the mid-troposphere resemble those at the few monitoring sites at the surface. The trends are huge: ~10% per decade at high latitudes and ~5% per decade over the mid-latitudes. Winds mix CO₂ throughout the atmosphere, albeit incompletely. The mid-tropospheric amplitude trends therefore signify an increasing NEP over a wide swath of the biosphere, with the increase fastest at high latitudes.

The question arises, what is causing the Northern Hemisphere land biosphere, especially at high latitudes, to go into hyperdrive? Surely, the biosphere must be enjoying the warming. Satellite observations show that from 1982 to 2011, the photosynthetic season has been lengthening over the past three decades: On average, the onset of greening of northern ecosystems (>45 N) has advanced by 1 day per decade in the spring, and the seasonally integrated photosynthesis has increased, consistent with the warming and thawing (3). However, enhanced photosynthesis alone is not enough to explain the large increase in CO₂ amplitude seen by Graven et al. The authors hypothesize that observed changes in the structure of the biosphere—for example, northward migration of the tree line, increased shrub cover in the Arctic, and reestablishment of forests after fires—have enhanced carbon uptake to the extent necessary to explain the amplitude trend.

The satellite data show that the photosynthetic season of northern ecosystems does Deeper breathing. The net ecosystem productivity (green) captures the seasonal uptake of carbon dioxide by the biosphere (A). Graven et al. have used aircraft data to determine how carbon dioxide concentrations have oscillated in the troposphere over recent decades. The seasonal oscillations are largest at high latitudes (B) than at mid- (C) and low-latitudes (D). The amplitude of this “breathing” is increasing, especially at high latitudes. [Panels B to D adapted from fig. 54 in (1)]