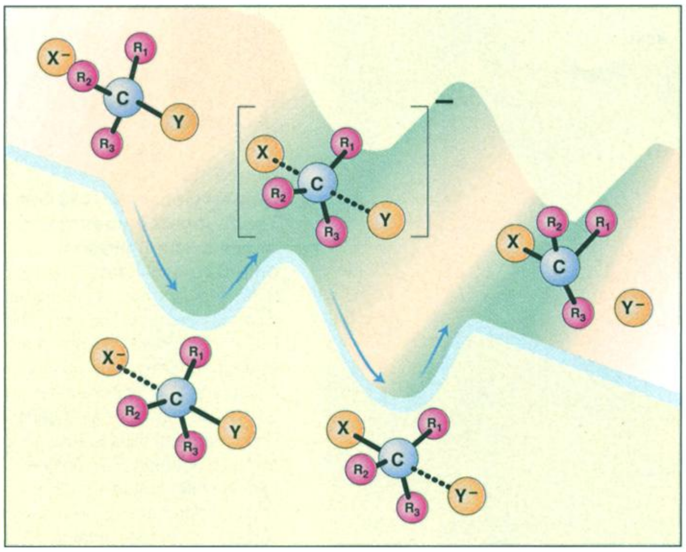

Schematic reaction coordinate for the S_N2 reaction. Repulsions between the R_1, R_2, and R_3 substituents in the transition state are responsible for the steric effect.

Unlike previous studies that made use of less sensitive experimental methods and were constrained to probe faster, exothermic reactions, Regan *et al.* examine an "identity" reaction, that is, the nucleophile and the leaving group are identical. This approach eliminates the need to remove the contribution of the reaction exothermicity to the measured steric barrier (*13*).

Identity reactions proceed at rates that are at most a few percent of the encounter-controlled rates characteristic of gas phase ion-molecule reactions. Fourier transform mass spectrometry methods that allow the necessary long observation times are therefore essential for reliable rate measurements. Regan *et al.* show that the intrinsic barrier height for chloride exchange in 2-chloro-3,3-dimethylbutyronitrile is 1.6 kcal/mol higher than in 2-chloropropionitrile. The magnitude of this intrinsic barrier increase (attributable to the increased steric effect as *t*-butyl is substituted for methyl on the reactive carbon center) is about one-quarter of the barrier increase observed in aqueous solution.

The authors augment this experimental determination with molecular dynamics simulations that evaluate the contribution of solvation effects to the free energy of activation. The calculations show that substitution of *t*-butyl for methyl at the reactive carbon results in a free-energy increase of 4 kcal/mol at the transition state. The total increase in the barrier height, 1.6 kcal/mol from the intrinsic barrier and 4 kcal/mol from solvation, is in good agreement with the 5- to 7-kcal/mol increase observed in aqueous solution.

The study provides a fundamental benchmark for quantitative understanding of the critical contributions that noncovalent interactions make to chemical reaction rates. The clear separation of functional group substitution into an intrinsic steric component and a contribution from solvation will lead to a deeper understanding of the fundamental relations among chemical structure, dynamics, and reactivity. The ability to optimize chemical reactions, develop new chemistry, and predict the properties of complex chemical systems will benefit all disciplines that work at atomic and molecular length scales.

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PERSPECTIVES: COSMOLOGY

The Beginning of Time

Craig J. Hogan

The Cosmic Background Explorer (COBE) satellite (*1*) scanned the farthest reaches of the sky for 4 years to assemble data for its historic map of primordial radiation. The blotchy pattern in the map (see the figure), which represents tiny variations in radiation brightness, is caused by small-amplitude perturbations in the structure of space-time that stretch across billions of light years of space today; they are the largest structures we will ever be able to see.

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It now seems likely that these structures may also be magnified images of the smallest things we will ever be able to see. The pattern is a faithful image of quantum fields—individual elementary particles whose imprint was frozen into the fabric of space-time very early and was then stretched to enormous size by cosmic expansion. Similar fluctuations led to the gravitational formation of all astronomical structure we see today, including our own Galaxy and its stars and planets.

In the last 2 years, experiments on high-altitude balloons circling Antarctica and in the high desert passes of the Andes have returned low-noise maps of smaller patches of sky than COBE, but with much finer angular detail than COBE's blurry 7° beam. A NASA spacecraft, the Microwave Anisotropy Probe (MAP), is now gathering data and should, within a year, return a detailed all-sky map at better than 1° resolution. The European PLANCK mission aims to create an even more detailed map with even higher accuracy a few years later.

The closer studies of the perturbations now under way are yielding precise measurements of the main global parameters of the universe and may provide concrete data on the long-sought connections between quantum mechanics and gravity (or the fields of mass-energy and the space-time within which they act).

The biggest and the smallest things in nature are connected by a set of ideas called inflationary cosmology (*2–5*). Physicists postulate that the dynamics of the early universe are controlled by a new field called the inflaton, whose behavior resembles that of the Higgs field, a central component of the Standard Model of particles and interactions. (The Higgs boson, although not yet directly observed, is responsible for the masses of elementary particles such as the electron, and some of its properties are already quite precisely known.)

For both fields, gravity can have the remarkable property of being repulsive rather than attractive. If the properties of the infla-

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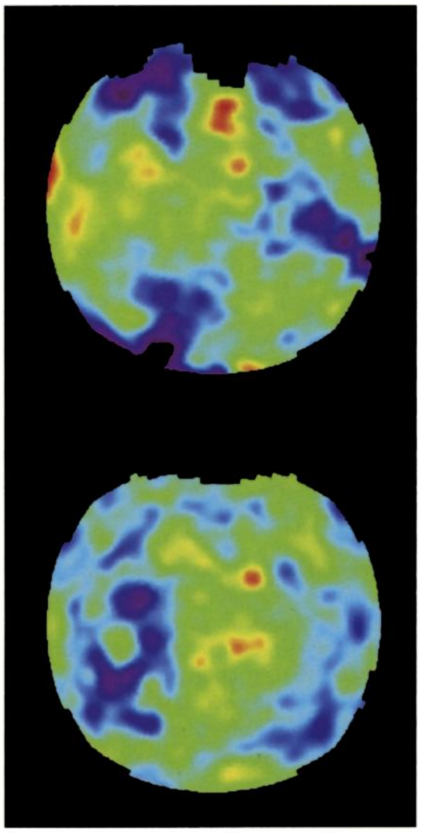
ton are set correctly, a system can be constructed that is dominated at first by repulsive gravity—leading to an exponentially expanding universe—and that gradually shifts to being dominated by more familiar forms of energy such as light and matter. These properties are just what we need to set up a large, nearly uniform, expanding universe like the one we live in. The simple, mechanistic model of inflation thus generates an enormous expanding universe, full of light and matter, from a tiny speck of unstable vacuum.

Inflationary universes are not exactly uniform, due to an interplay between the gravity-driven expansion and quantum mechanics. Quantum fields can be viewed as waves or as collections of fuzzy particles, whose size ℓ and energy E are related by $E \approx hc/\ell$, where h is Planck's constant and c is the speed of light. In the accelerating, inflationary universe, there is a certain critical particle size c/H called the Hubble length (H is the "Hubble constant" or expansion rate at that time). Particles much smaller than c/H do not notice the expansion much and act like quantum fields do in the laboratory, in which the vacuum creates and destroys quanta on all scales, all the time, creating a roiling sea of vacuum fluctuations. Particles bigger than c/H fly apart faster than the speed of light, so they cannot fluctuate; they are "frozen in" to the expansion.



Signs of inflation. This sky map of cosmic background radiation temperature covers most of the northern and southern Galactic hemispheres, as viewed from the local cosmic standard of rest. The hottest/coldest spots have temperatures about 100 microkelvin above/below the mean value of 2.725 K. The pattern is consistent with random noise, but it is not white noise: the correlated structures stretching across the sky are real. According to inflationary cosmology, they originated as elementary particles.

It is the vacuum fluctuations near the Hubble scale that give rise to the features in the COBE map, and to all cosmic structure. The fields are caught in the act of fluctuating by the expansion as they are stretched beyond the Hubble length. They start out as quanta of inflatons or gravitons with microscopic energy $E \approx hH$, but are then hugely amplified as they are stretched along with the inflating universe. The inflating universe thus acts like a quantum-noise-limited amplifier, and the Hubble-length perturbations are the quantum noise.

These frozen-in perturbations become flaws in the nearly uniform gravitational fabric of the expanding universe. On the largest scales, such as the COBE map, the imprint of the primordial field maps fairly directly into microwave background anisotropy. On scales a thousand times smaller, the flaws in the expansion lead to gravitational collapse and formation of galaxies.

Perturbations over a range of intermediate scales also excite acoustic waves in the coupled photon-baryon plasma of the early universe at redshifts of a few thousand that leave distinctive signatures in the anisotropy spectrum, allowing precise measurements of cosmological parameters such as baryon density and the global geometry of space (*6*). A new generation of experiments, including the MAP spacecraft (*7*), will measure many cosmological parameters (and some properties of the inflaton) with high precision, and may even disentangle the contributions of graviton and inflaton quanta by measuring the polarization of the anisotropy (*8*).

By dealing with the creation of the universe, inflation theory is also expanding the scope of scientific cosmological debate. The interpretation of the quantum state of the whole universe, or of its initial state, is no longer entirely philosophical. The idea of a "multiverse," a multiplicity of big bangs, is a natural feature of many inflationary models (*9*). Multiple universes even have concrete applications, for example, in the theory of a hypothetical dark matter particle called the axion. The physical density of axion particles created in the early universe can be determined by a random process, which sets different densities among the various big bangs in the multiverse ensemble.

Inflationary perturbations also probe new physics beyond the inflaton (*10*). Some studies consider the residual "memory" of a time when quanta were much smaller than the Planck scale, well into the domain of quantum gravity; others consider the impact of possible extra dimensions, or even reinterpret the inflaton as an extra spatial dimension with new dynamics.

One of the most intriguing possibilities starts with a conjecture in quantum gravity, first derived from the thermodynamics of black hole evaporation, called the "holographic principle" (*11*): everything happening in any three-dimensional volume can be specified by a finite quantity of information proportional to the area of its two-dimensional bounding surface. The world in this view is like a hologram: physics looks three dimensional but is really happening on a two-dimensional projective surface. Furthermore, it looks continuous, but on closer examination is really discrete.

The holographic principle limits the amount of information carried by quanta during inflation to less than π/H^2 in Planck units. This bound is greater than about 10^{10} bits, but it is certainly not infinite; indeed, the amount of information needed to specify literally everything during inflation may be small enough to fit onto a compact disc. The universe thus began with rather little information, and practically all the complex structure we see now developed from within in the absence of external influences. Entire galaxies developed from almost structureless single quanta.

If the holographic conjecture is correct, then inflaton quanta may display discreteness (*12*) observably different from the standard prediction of a continuous noise field. The inflationary epoch would mark the boundary where the familiar picture of quantum fields moving in four-dimensional spacetime starts to pixelate into the new transcendent degrees of freedom of a new, quantum-mechanical theory of gravity and matter. We might, in a technical sense, soon observe the beginning of time.

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