

PERSPECTIVES

On a typical day. (Right) Schematic vertical section from equator to pole on a particular day, showing the tropopause with westerly jet streams, tropical convection, and transport and exchange. **(Left)** Typical vertical profile of atmospheric temperature.

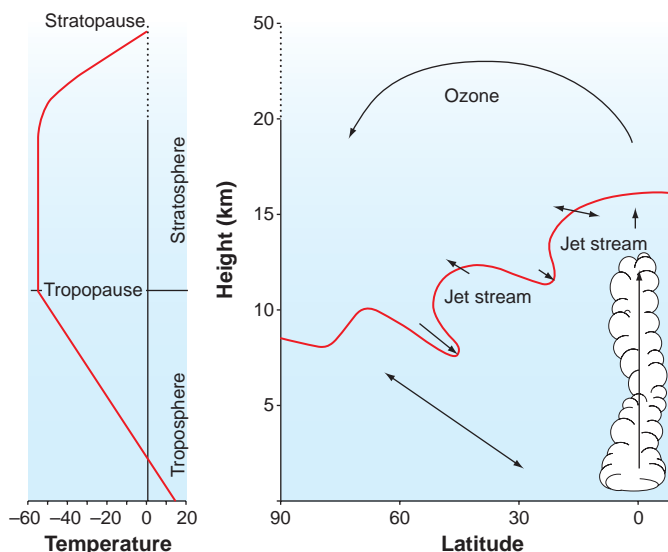
the upper troposphere and of the different concentrations of radiatively important trace constituents on the two sides. The lower stratosphere contains much more ozone, but the troposphere is much moister.

The tropopause typically slopes from about 9 km near the poles to about 18 km near the equator. However, because it is distorted by weather systems, on any particular day and longitude the tropopause is likely to be far from smooth, with thin tongues of stratospheric air sometimes moving deep into the troposphere (4).

The tropopause is important on a daily basis because it puts a lid on tropospheric convection. It also plays a very active role in the development of large weather systems: One classic view of the growth of weather systems involves the interaction of waves propagating on temperature gradients at the tropopause and at Earth's surface (5).

Not only the amounts of trace chemicals but also the dominant chemical processes differ widely in the regions on either side of the tropopause. For these reasons, there has been much interest in the extent to which the tropopause is permeable, allowing stratosphere-troposphere exchange (6). Such exchange influences stratospheric ozone reduction, tropospheric pollution, and global warming.

The tropospheric air that eventually moves high into the stratosphere crosses



the tropopause in the equatorial region. The extreme dryness of the stratosphere suggests that this must occur mainly over the Indonesian region, where the temperature is low enough to “freeze-dry” it. However, the winds are such that while the air crosses the tropopause it must also move a considerable horizontal distance. A picture of the three-dimensional motion in this region is starting to emerge (7). In the subtropics, there is two-way exchange, whereas at higher latitudes, streamers and cut-off pools of stratospheric air are produced by weather systems and later absorbed into the troposphere (8).

On the basis of the contrasting thermodynamic budgets of the weather-dominated troposphere and radiation-dominated stratosphere, the height of the tropopause can be estimated (9, 10). More simply, assuming that the vertical temperature profile is like that shown in the figure and that the lapse rate in the troposphere does not change, tropopause height changes are related to changes in tropospheric and lower

stratospheric temperatures. An increase in the former and a decrease in the latter—as expected, for example, with increases in carbon dioxide concentrations—both lead to a higher tropopause. In each case, a 1°C change leads to a rise in the tropopause by about 160 m. Stratospheric ozone reduction also leads to stratospheric cooling and, hence, a higher tropopause. In contrast, sulfate aerosols are calculated to cool the troposphere and therefore lower the tropopause. Other natural and anthropogenic forcings will also act to change its height.

The analysis of Santer *et al.* suggests that over the past 20 years, the observed globally averaged tropopause height has risen by ~200 m. Their model results show that this rise is consistent with the changes in natural and anthropogenic forcings over this period, and that greenhouse gas and ozone changes are mostly responsible for it. Continuing changes in the properties of the tropopause as a result of human activity could have wide-ranging implications because of its physical and chemical roles in the climate system.

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CHEMISTRY

Colloidal Molecules and Beyond

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About a hundred years ago, Jean Perrin's experiments on colloids—particles a few nanometers to a few micrometers in diameter—convinced even the skeptics that matter consists of atoms and molecules. More recently, the analogy between atoms and colloids has led to in-

sights into crystal nucleation and growth, the glass transition, and the influence of the range of particle-particle interactions on phase behavior. Moreover, the ability to manipulate colloid crystallization has led to advanced materials such as photonic crystals.

To date, most studies of colloids have used spherical particles or particles with simple shapes, such as rods and plates. Syntheses of nonspherical colloids gener-

ally yield a broad size distribution. On page 483 of this issue, Manoharan *et al.* (1) report a method for making large quantities of identical colloidal particles with complex shapes consisting of equal-sized colloidal spheres.

The authors made these particles by drying the oil out of an oil-in-water emulsion in which spherical colloids were adsorbed to the surface of the oil droplets. Subsequent centrifugation yielded an intriguing sequence of colloidal structures (including the tetrahedral tetramer in the top left panel of the figure). Each structure consists of 2 to 15 spheres. For a given particle size, the spheres are arranged identically in all particles (1).

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The smaller structures of the sequence—dumbbell, triangle, tetrahedron, triangular dipyramid, and octahedron—have all been observed in molecules, complexes, or clusters. The new colloids thus substantially broaden the range of colloidal molecule analogs. By altering the salt concentration in the liquid or applying an external electric field, the interactions between the colloidal molecules can be further tuned, thereby further increasing the range of possible colloidal structures.

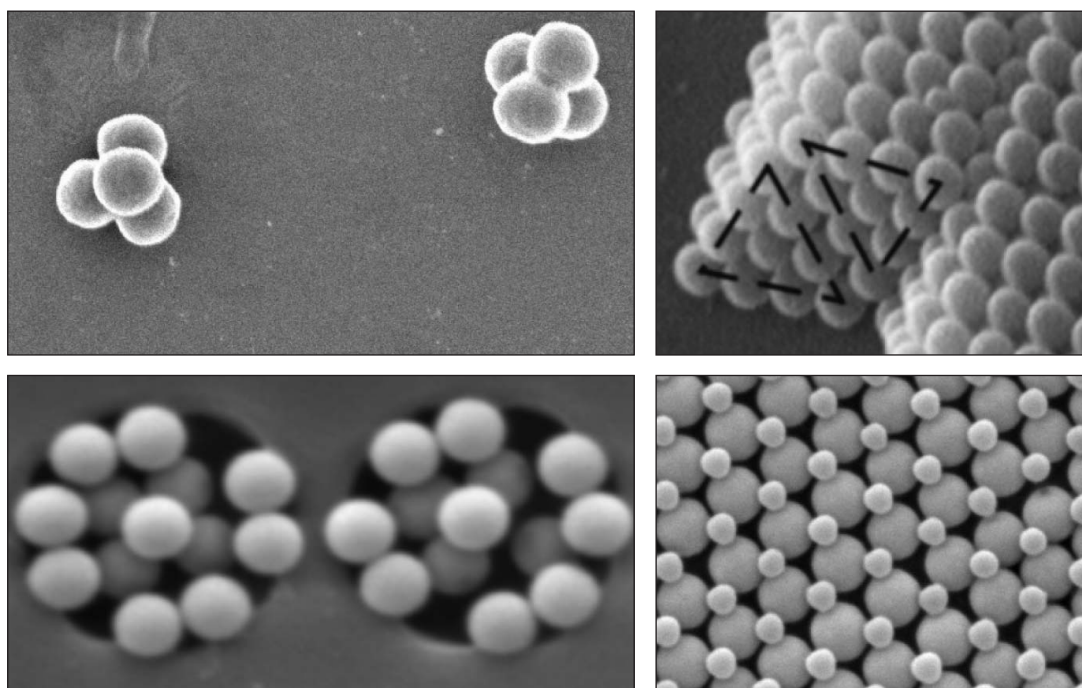
Because the method of Manoharan *et al.* yields large quantities of colloidal molecules in pure form, their phase behavior and glass transition can be investigated. This will shed light on fundamental condensed-matter issues and

will lead to new colloidal crystal structures. For instance, making 3D photonic crystals with a band gap in the visible spectrum, a goal that has not yet been achieved, would be much easier if colloids could form crystals with a diamond lattice (8). Tetrahedral colloids (see the figure, top left) might do just that.

Perrin proved the atomic reality of matter with colloidal spheres. The results of Manoharan *et al.* have now brought the investigation of the collective behavior of more complex colloidal molecules within reach. Because the method requires stability of the initial colloidal spheres in both the oil and the water phase, it will not be easy to extend the method to colloids with different compositions. But the exciting prospects for model studies and new materials will provide a strong impetus for many groups to try.

References

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Packing spheres under different constraints. (Top left) Tetrahedral clusters of tetramers are formed by drying spheres attached to emulsion droplets (1). (Top right) A prism phase results from packing spheres between two walls (6). (Bottom left) Holes in a polymer layer act as containers in which spheres collect. Subsequent drying creates composite particles like those of Manoharan *et al.* (1). (Bottom right) A regular arrangement of small spheres on large spheres results from drying in a layer-by-layer fashion (7).

The drying of droplets has been used before to arrange colloidal particles into new structures. Velev *et al.* dried droplets of a colloidal dispersion on top of an oil phase (2). The final structure consisted of round colloidal crystals about 0.5 mm in diameter that contained many particles. More recently, Weitz *et al.* used attractive forces to cement spheres adsorbed on the interface of a water-in-oil emulsion together before drying out the water (3). The resulting hollow particles do not contain the same number of spheres, nor do they have exactly the same arrangement of spheres.

Colloidal particles have also been dried in confined geometries, such as those formed by a two-dimensional (2D) array of surface patterns (4, 5) (see the figure, bottom left). However, this method yields much fewer particles than the method of Manoharan *et al.* (10^5 compared with 10^{10}), and is difficult to scale up; about 10% of the particles are defective (4).

In the method of Manoharan *et al.*, it is essential that the colloids are stable both in the oil and in the water phase. This ensures that the composite particles do not aggregate while drying. After drying is complete, the particles are held together by strong van der Waals forces. However, during drying, the spheres do not come together in a random aggregation process; if they did, then the particles would not all

have the same shape. What drives the packing is not completely understood.

Mathematical theories of the packing of spheres find application in fields such as error correction and data compression. Only 6 years ago, it was proven that the densest way in which spheres can be arranged in three dimensions (3D)—also known as Kepler's problem—is in stacks of hexagonal layers. External constraints also affect sphere packings. For example, the packing of colloidal spheres between two walls results, for certain wall separations, in prism-shaped structures (see the figure, top right) (6). Other constraints, such as minimizing the volume or optimizing the energy of spheres that attract each other at short distances, yield different structures.

Manoharan *et al.* could find no constraint, however, that leads to exactly the observed sequence of structures. The key factor may be the minimization of the total surface area of the drying liquid between the spheres. In an earlier 2D study, the drying of particles onto a hexagonal layer of larger spheres led to unexpected arrangements of spheres (see the figure, bottom right) that were attributed to such a drying film (7). Theoretical work on this complicated geometrical problem is needed to determine whether this constraint can indeed lead to the observed sequence of sphere packings.