

Field-Induced Layering of Colloidal Crystals

M. Trau, D. A. Saville, I. A. Aksay*

An electrohydrodynamic methodology has been developed that makes possible the precise assembly of two- and three-dimensional colloidal crystals on electrode surfaces. Electrophoretically deposited colloidal particles were observed to move toward one another over very large distances (greater than five particle diameters) to form two-dimensional colloidal crystals for both micrometer- and nanometer-size particles. This coalescence of particles with the same charge is opposite to what is expected from electrostatic considerations and appears to result from electrohydrodynamic fluid flow arising from an ionic current flowing through the solution. The ability to modulate this "lateral attraction" between particles, by adjusting field strength or frequency, facilitates the reversible formation of two-dimensional fluid and crystalline colloidal states on the electrode surface. Further manipulation allows controlled structures to be assembled.

The controlled assembly of materials with patterned structural features on submicrometer length scales, "nanostructured materials," is a rapidly expanding area in materials science (1). In particular, multilayered nanocomposites, typically formed by molecular vapor deposition, exhibit macroscopic properties that are remarkably different from those of more conventional engineering materials, whose structural features lie in the micrometer-size range or greater (2). Although nanostructured materials display considerable potential, their development is currently hindered by an inability to conveniently and economically form such materials in large quantities, preferably under ambient conditions. As an alternative to molecular vapor deposition, which uses individual molecules as building blocks, we propose the assembly of macromolecular building blocks (such as colloids and proteins) to form designed structures on larger length scales by electrophoretic deposition. The assembly of colloids into patterned structures has heretofore been achieved by dispersing monosized colloidal particles in a solvent and allowing crystalline regions to form as a result of specific particle-particle interaction forces or entropic effects (3). The formation of such colloidal crystals is difficult to regulate externally and is cumbersome to confine to two dimensions so as to process "designed" multilayers (4). For similar reasons, protein crystallization is difficult to regulate and is currently the rate-determining step in the determination of the structure of biologically important proteins (5). Here we report on a method that allows layer-by-layer deposition of colloidal crystals through electrohydrodynamic manipulation.

To observe the deposition mechanism in detail, we used an optically transparent in-

dium tin oxide (ITO) electrode coupled to an optical microscope (Fig. 1). To illustrate the phenomenon by optical microscopy, we used large particles. Similar results were obtained with nanometer-size particles (see below). Examples of electrophoretic deposition onto an ITO anode with our technique are shown in Fig. 2 for submonolayer, electrophoretically deposited films of silica [Fig. 2A; 900 nm in diameter (Bangs Laboratories)] and polystyrene [(PS) Fig. 2D; size standards 2 μm in diameter (Duke Scientific)] particles from a dilute suspension. With silica, the suspending fluid was triply distilled water (pH = 5.8 with a conductivity of $<1 \mu\text{S cm}^{-1}$); for PS the ambient fluid contained a mixture of ionic and non-ionic surfactants (Duke Scientific) added to provide the colloidal stability. Two-dimensional (2D) "gaseous" structures (Fig. 2, A and D) form upon application of a weak electric field (for example, 0.5 V) across the dilute suspension or when the particles settle onto the electrode. In neither case do the particles adhere to the electrode surface; instead, they continue to move in two dimensions through Brownian agitation.

The 2D mobility of these particles in the presence of an electric field is surprising, given the large electrostatic attraction between negatively charged particles and a positively charged electrode. This effect appears to be a consequence of steric stabilization. For our PS particles, stabilization was provided by an adsorbed surfactant layer on the surface of the particles. With the silica particles, no surfactant was added to the solution, and it is probable that the particles remain stable because of the presence of polysilicate moieties at the silica-aqueous solution interface. The existence of such polysilicate moieties, "stubble hair," on the silica surface has been shown to cause a short-range repulsive force between silica surfaces (6, 7).

Increasing the applied voltage (for example, from 0.5 to 1.5 V) caused surprising

responses (see Fig. 2, B, C, E, and F). With a sufficiently strong current, the particles move toward one another across the electrode surface. This "lateral attraction," first observed by Richetti *et al.* (8), acts normal to the applied field and is strong enough to bring particles together to form stable, 2D colloidal crystals. However, no detailed understanding of the underlying mechanism was achieved. At field strengths of 50 to 100 V cm^{-1} (1 to 2 V applied, $\sim 100 \mu\text{A cm}^{-2}$), crystal formation is reversible. When the field is removed, particles are stirred by Brownian motion to form 2D "gaseous" structures similar to the ones shown in Fig. 2, A and D. One can adjust the strength of the lateral attraction between particles by changing the magnitude of the current. Modulation of the strength of the particle-particle interaction allows the formation of different 2D "gas," "liquid," and crystalline colloidal phases on the electrode. Phase transitions can be easily induced by varying the current. The lateral attraction also acts when an ac voltage is applied, as long as the frequency is not too high. The 2D colloidal phase transitions are observed when the amplitude of the applied ac or dc voltage is gradually increased. Above a frequency of 1 MHz, the attraction disappears.

To investigate the deposition mechanism of nanometer-size particles too small to be imaged by optical microscopy, we performed deposition experiments with 16-nm gold particles, following the method reported by Giersig and Mulvaney (9). Gold particles synthesized according to the method of Turkevich *et al.* (10) were electrophoretically deposited onto a carbon-coated electron microscope grid. After deposition, the films were removed from solution, dried, and imaged with transmission electron microscopy (TEM). A typical example of a submonolayer film of particles formed

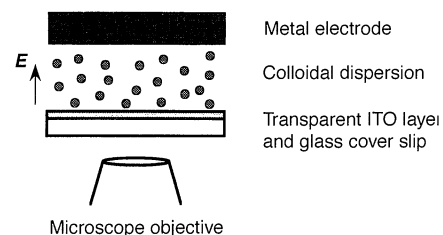


Fig. 1. Diagram of the apparatus. An ITO-coated microscope cover slip (resistivity, 60 ohms per square) forms the anode, and a piece of polished brass (2 cm by 2 cm) forms the cathode of an electrolytic cell. These are separated by an insulating Teflon spacer 0.2 mm thick, and the thin cavity is filled with a colloidal dispersion. Upon application of an electric field E , particles are observed through the transparent electrode by means of an optical microscope (Leitz Metallvert). Particle motion is recorded on video tape.

Department of Chemical Engineering and Princeton Materials Institute, Princeton University, Princeton, NJ 08544, USA.

* To whom correspondence should be addressed.

in this way is shown in Fig. 3. The formation of 2D clusters, similar to those shown in Fig. 2, reveals the existence of a lateral attraction operating in a manner similar to that observed for larger particles (11). Lateral attraction during electrophoretic deposition is a general phenomenon that operates for any colloidal material that remains colloidally stable at the electrode-solution interface.

Attraction between electrophoretically deposited particles at the electrode interface is surprising, given the strong repulsion expected from purely electrostatic forces. All of the particles are similarly charged and have a diffuse ion cloud (double layer) that is polarized by the electric field. Accordingly, some electrostatic repulsion from monopole and dipole interactions is present as particles approach each other, so the observed attraction is clearly not the result of a simple electrostatic interaction. Whatever the attractive interaction, it must be strong enough to overcome electrostatic repulsion.

The attractive interaction appears to result from electrohydrodynamic effects arising from charge accumulation near the electrodes due to the passage of ionic current. The currents in our system are between 1 and 500 $\mu\text{A cm}^{-2}$, depending on the applied voltage and the time required to reach steady state, and they result from the electrolysis of water. Bubble formation was not observed under our experimental conditions because current densities were low, $<1 \text{ mA cm}^{-2}$, which allowed H_2 and O_2 reaction products to be solubilized in the bulk solution and transported away from the electrode surface (12). Electrolysis produces H_3O^+ ions at the anode and OH^- ions at the cathode, and, with background electrolyte concentration present (for ex-

ample, due to dissolved CO_2), ionic conduction occurs primarily through electromigration of the electrolyte species. Provided the fluid remains motionless, the passage of current leads to a buildup of ions in the vicinity of the electrodes, a process known in electrochemistry as "concentration polarization" (13). The accumulation of ions near the electrode sets up a pressure gradient in the fluid because coulombic forces, which act on regions of fluid near the electrode where there is an ionic space charge, are balanced by pressure gradients so as to maintain equilibrium. Given the planar symmetry of the two-electrode system, the induced pressure gradient is uniform in directions parallel to the electrodes. However, the planar symmetry is interrupted by the presence of particles. Our model of the phenomenon of attraction is as follows.

Concentration polarization occurs on a length scale that is directly proportional to the ionic strength and ion mobility and inversely proportional to the current. At conditions representative of our work, this length scale is a few micrometers. However, the thickness of the concentration polarization layer varies laterally because of the alteration of the current arising from particles near the cathode. Lateral variations in the amount of concentration polarization induce a spatially varying "free charge," and the action of the electric field on the free charge induces fluid motion. This electrohydrodynamic motion and the associated pressure field cause the particles to move toward one another. Because the induced charge is proportional to the applied field (or current), motion can be induced by either dc or ac fields, as long as the frequency is not too high. Hydrodynamic calculations based on this model show that, al-

though the convection cells fill the space between the electrodes, they are weak outside the polarization layer. To check the quantitative features of our electrohydrodynamic model, we performed experiments with a patterned electrode. The flows observed were in accord with our model (14).

Another example of this phenomenon is

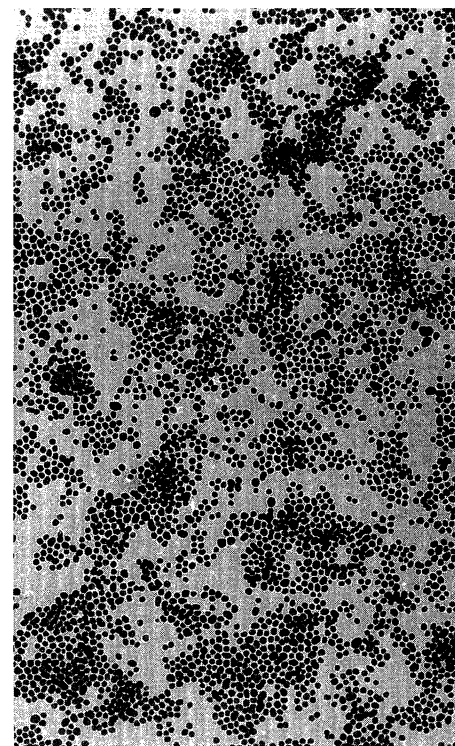


Fig. 3. TEM image of a submonolayer of gold particles (mean particle diameter, 16 nm) electrophoretically deposited onto a carbon-coated copper grid by application of a field of 0.3 V cm^{-1} for 300 s. The extensive clustering of particles reveals the existence of a lateral attraction operating in a manner similar to that observed for larger particles (Fig. 2).

Fig. 2. Two examples of the long-range "lateral attraction force" that acts during electrophoretic deposition. (A to C) Silica particles 900 nm in diameter electrophoretically deposited onto the transparent anode with the applied voltage controlled (from 0 to 2 V) to maintain a constant current of $40 \mu\text{A cm}^{-2}$. The applied electric field restricts the particle motion to two dimensions on the surface of the electrode, whereupon a long-range ($>$ five particle diameters) attractive force pulls the particles together to form 2D crystals. (D to F) PS particles $2 \mu\text{m}$ in diameter deposited by application of a constant voltage (2 V). Long-range lateral attraction forces cause the larger polystyrene particles to aggregate into 2D crystals. The time elapsed between successive frames is $\sim 15 \text{ s}$. No field was applied in (A) and (D). Manipulating the current density changes the magnitude of the lateral attraction, allowing the formation of different 2D colloidal phases, such as gas, liquid, and solid, on the surface of the electrode.

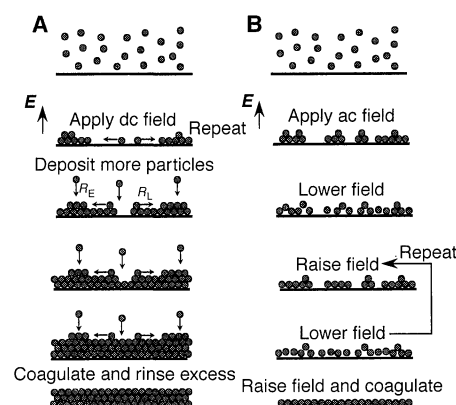
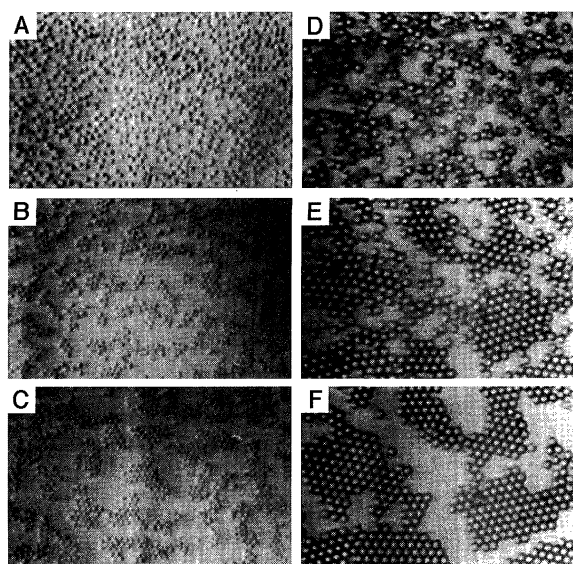


Fig. 4. Two methods of assembling colloidal particles into ordered multilayers: (A) particle assembly with a dc field, and (B) particle assembly with a low-frequency ac field. Both techniques deliberately use the lateral attraction force displayed in Fig. 2 to form highly ordered structures.

seen during electroplating reactions, where convective currents are frequently observed and result in patterned blemishes on the plated surface (15). Once fluid is set in motion, the situation becomes more complex because the space charge distribution is affected by this motion. This electrohydrodynamic mechanism fits qualitatively with the observed long-range nature of the lateral attractive force. It also conforms with another of our experimental observations: the migration of particles toward macroscopic scratches and defects in an ITO electrode (14).

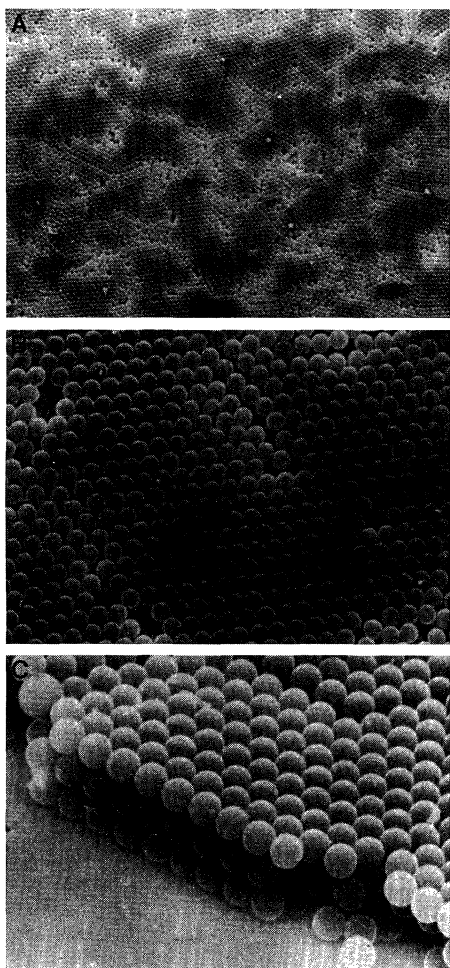


Fig. 5. Scanning electron microscope images of a multilayered colloidal crystalline film made by assembling and coagulating 2- μm PS colloidal particles according to the scheme shown in Fig. 4A. The particles were deposited by the application of an electric field of 40 V cm^{-1} (2 V applied) for 40 min with a dispersion of the PS particles. The current density during most of this period was $\sim 100 \mu\text{A cm}^{-2}$. To coagulate the first three layers, we left the field on for 12 hours after the assembly process was complete. Then, particles not coagulated by the field (that is, particles in the fourth or higher layers) were rinsed away with distilled water. (A and B) The surface of the film at two different magnifications. (C) A cross-sectional view revealed by scratching a portion of the film with a sharp needle.

External control of the magnitude of the lateral attraction force between electrophoretically deposited particles allows the controlled assembly of highly ordered mono- and multilayers of colloidal particles. We used two assembly procedures which use the lateral attraction force (Fig. 4). With the dc-field assembly the total number of dispersed particles was far greater than that required to form a monolayer (Fig. 4A). The dc electric field was adjusted so that the rate of arrival of particles through electrophoretic deposition, R_E , was slow relative to the rate of lateral motion of particles toward other particles on the surface, R_L , due to the lateral attraction force. The quantity R_E depends mainly on the particle charge and the magnitude of the electric field in the bulk solution; R_L depends mostly on the current density passing through the particle layer. When $R_L \geq R_E$, highly ordered multilayered films may be grown with large ordered domains. A three-layer film of PS particles, assembled in ~ 40 min at 2 V, is shown in Fig. 5. Manipulation of the R_L/R_E ratio, that is, changing the "quenching rate" of the assembly process, controls the size of the domains, thereby allowing formation of a variety of packing geometries, from amorphous to highly crystalline. Similar multilayered structures have been formed with the silica particles shown in Fig. 2.

Once the crystalline structures have been assembled, they may be permanently "frozen" if one induces controlled coagulation with the applied field. For example, a strong dc voltage ($> 2 \text{ V}$) compresses the particles in the direction of the field and they coagulate or adhere to the electrode surface. When a large-amplitude ac voltage (for example, 1 kHz, 5 V) is applied, the particles experience no net electrostatic force pulling them toward the electrode, but they are pushed together by electrohydrodynamic effects. With the ac field, particles coagulate, with little or no adhesion to the electrode. This method of controlled coagulation allows the removal of a coagulated sheet of colloidal material, either electrophoretically, by reversing the polarity of the electrodes, or by flow. We caused the layered structure shown in Fig. 5 to coagulate by leaving the applied voltage at 2 V for 12 hours after the multilayer had assembled. Coagulation of the first layer onto the electrode surface is achieved relatively quickly (< 1 min for voltages $> 2 \text{ V}$); however, coagulation of higher layers is more difficult and requires higher applied voltages and longer coagulation times.

Another method of monolayer assembly is shown in Fig. 4B. This method is particularly suited for the sequential assembly of multilayered colloidal structures with alternating composition. Here, the exact num-

ber of particles required to form a fully dense monolayer on the surface is dispersed in the suspension and electrophoretically deposited onto the electrode in a random arrangement similar to that shown in the first step of Fig. 4A. Next, the applied field strength is lowered until Brownian agitation begins to fluidize the colloidal layer, that is, until the 2D crystal structures in the first layer begin to melt and form liquid or gaseous phases. After the particles randomize by Brownian motion, the applied voltage is raised until the particles in the first layer crystallize. At this point, a certain number of particles previously in the second layer have been transferred to the first layer, and a new crystal structure is formed. This process is repeated until all of the particles in the second, or higher layers, have been transferred to the first layer. For our 2- μm PS particles, this is usually achieved by the application of a low-frequency ac offset voltage (for example, 0.02 Hz at 0.2 to 2 V peak to peak) for ~ 20 min. These monolayers have packing geometries similar to the surface layer shown in Fig. 5, but the domain sizes are smaller because of the many randomization steps. The procedure, "field-induced annealing," has the effect of sequentially melting ("shaking") and freezing the crystallized colloidal layer until all of the particles are present in the required packing arrangement. The kinetics of the process, that is, the duration of the shaking step compared with the duration of the freezing step, determines the domain size of the 2D crystals in the monolayer.

The controlled assembly and coagulation of colloidal particles into patterned structures through electrophoretic deposition offers a simple method for the construction of materials with designed microscopic architectures. The simplicity of this technique as compared to molecular vapor deposition methods makes it very attractive as a route to economically manufactured nanostructured materials. Furthermore, this method may also be suitable to assemble macromolecules such as proteins into 2D crystals and other patterned structures.

REFERENCES AND NOTES

1. G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **254**, 1312 (1991); J. M. Schnur, *ibid.* **262**, 1669 (1993); R. W. Siegel, *Phys. Today* **64**, 64 (1993); H. Masuda and K. Fukuda, *Science* **268**, 1466 (1995); E. Kim, Y. Xia, G. M. Whitesides, *Nature* **376**, 581 (1995).
2. T. Tsakalakos and J. E. Hilliard, *J. Appl. Phys.* **54**, 734 (1983); A. F. Jankowski, *Nanostructured Mater.* **6**, 179 (1995); M. Gell, *J. Min. Met. Mater. Soc.* **46**, 30 (1994).
3. P. Pieranski, *Contemp. Phys.* **24**, 25 (1983); P. N. Pusey and W. van Megan, *Nature* **320**, 340 (1986); D. J. W. Aastuen, N. A. Clark, L. K. Cotter, B. J. Ackerson, *Phys. Rev. Lett.* **57**, 1733 (1986); K. Schatzel and B. J. Ackerson, *ibid.* **68**, 337 (1992); W. van Megan and S. M. Underwood, *Nature* **362**, 616

- (1993); T. Okubo, *Langmuir* **10**, 1695 (1994).
4. G. Y. Onoda, *Phys. Rev. Lett.* **55**, 226 (1985); D. H. Van Winkle and C. A. Murray, *Phys. Rev. A* **34**, 562 (1986); R. G. Freeman *et al.*, *Science* **267**, 1629 (1995).
 5. A. McPherson, *Preparation and Analysis of Protein Crystals* (Wiley, New York, 1982); G. Kolata, *Science* **229**, 370 (1985); F. Rosenberger, *J. Cryst. Growth* **76**, 618 (1986).
 6. T. W. Healy, *Adv. Chem. Ser.* **234**, 146 (1994).
 7. G. Vigil, Z. Xu, S. Steinberg, J. Israelachvili, *J. Colloid Interface Sci.* **165**, 367 (1994).
 8. P. Richetti, J. Prost, P. Barois, *J. Phys. Lett.* **45**, L-1137 (1984); F. Richetti, J. Prost, N. A. Clark, in *Physics of Complex and Supramolecular Fluids*, S. A. Safran and N. A. Clark, Eds. (Wiley, New York, 1987), p. 387.
 9. M. Giersig and P. Mulvaney, *J. Phys. Chem.* **97**, 6334 (1993); *Langmuir* **9**, 3408 (1993). These re-

- searchers observed the formation of 2D colloidal clusters and monolayers; however, they did not postulate a mechanism for the lateral attraction of particles on the electrode surface.
10. J. Turkevich, P. C. Stevenson, J. Hillier, *Discuss. Faraday Soc.* **11**, 55 (1951).
 11. Extensive 2D clustering of these gold particles is not possible through capillary aggregation mechanisms that occur during drying. These mechanisms always result in patchy, more irregular structures, as has been demonstrated by J. Liu, W. Y. Shih, M. Sarikaya, and I. A. Aksay [*Phys. Rev. A* **41**, 3206 (1990)] and control experiments performed by us.
 12. J. O. Bockris and S. U. M. Khan, *Surface Electrochemistry: A Molecular Level Approach* (Plenum, New York, 1993).
 13. V. G. Levich, *Physicochemical Hydrodynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1962).
 14. Our results on a quantitative calculation of the flow

- field resulting from lateral current gradients that exist on the surface of the electrode as a result of either electrodeposited colloidal particles or scratches or defects in the ITO layer will be published elsewhere (M. Trau, D. A. Saville, I. A. Aksay, unpublished results).
15. V. Fleury, J. H. Kaufman, D. B. Hibbert, *Nature* **367**, 435 (1994); M. Wang, W. J. P. van Enkevort, N. Ming, P. Bennema, *ibid.*, p. 438; C. Livermore and P. Wong, *Phys. Rev. Lett.* **72**, 3847 (1994).
 16. This work was supported by the U.S. Air Force Office of Scientific Research and the Microgravity Science and Applications Division of the National Aeronautics and Space Administration. Partial support for M.T. was provided by the Fulbright Commission. We acknowledge discussions with A. B. Bocarsly.

29 January 1996; accepted 13 March 1996

Galileo Gravity Results and the Internal Structure of Io

J. D. Anderson, W. L. Sjogren, G. Schubert

Doppler data generated with the Galileo spacecraft's radio carrier wave were used to measure Io's external gravitational field. The resulting triaxial field is consistent with the assumption that Io is in tidal and rotational equilibrium. The inescapable conclusion is that it has a large metallic core. If the core is a eutectic mixture of iron and iron sulfide, it comprises 20.2 ± 7.4 percent of the satellite's total mass with a radius that is about 52 percent of Io's mean radius of 1821.3 kilometers; if the core is pure iron, it comprises 10.5 ± 3.7 percent of the total mass with a radius of about 36 percent of the mean radius.

Jupiter is the largest planet in the solar system, almost 318 times more massive than Earth. Its gravitational field dominates the forces on its four largest satellites, discovered by Galileo in 1610. Io, its innermost Galilean satellite, is in orbital resonance with two other Galilean moons, Ganymede and Europa, and as a consequence, the tides raised on Io by Jupiter frictionally heat the satellite and produce an enhanced surface heat flow and active volcanic plumes (1). Io is covered by flows of sulfur, sulfur compounds, and silicates. Its mean density of 3529 kg m^{-3} and rugged topography suggest an interior composed of silicates, similar to the interiors of the Earth and its moon, as well as heavier metals.

Io is roughly the same size as Earth's moon (mean radius of 1821.3 km, compared with a lunar radius of 1738 km); however, its proximity to Jupiter and its rapid rotation (period of 1.769 days, compared with the lunar rotation of 27.3217 days) distinguishes it from our moon. Most significantly, the rotational and tidal forces on Io are 220 times larger than similar forces on Earth's moon. Consequently, although it is

incorrect to assume that Earth's moon can be approximated by a fluid body in hydrostatic equilibrium, it is a good first-order approximation for Io. Deviations from equilibrium, which are responsible for frictional heating, are of higher order and are not directly detectable from flyby data.

All this was known before the Galileo mission from a combination of ground-based observations and data from the Pioneer and Voyager missions to Jupiter. However, no other spacecraft had flown as close to Io as did the Galileo spacecraft on 7 December 1995 (2). By analyzing radio Doppler data generated during the flyby, we measured the tidal component of Io's gravitational field (Fig. 1), and by interpreting this measurement under the assumption of rotational and tidal equilibrium, we modeled the interior structure of the satellite. These results are relevant to studies of solar system formation and comparative planetology, including that of Earth. The interior properties that we determined can be combined with previously known surface properties to gain a better understanding of how Io evolved and how it reached its present state. For example, the surface observations tell us that sulfur is present in abundance, and volcanic activity tells us that it is abundant in the interior as well. The Galileo discovery that Io has a large metallic core suggests that iron and, because

of the abundance of sulfur, iron sulfide have separated from the lighter silicates to produce a differentiated satellite. Io must have been heated sufficiently during its evolution for differentiation to have occurred.

Io and Earth are the only bodies in the solar system for which a metallic core has been detected directly, by means of seismic waves for Earth and measurements of the gravitational field for Io. Given their relative locations in the solar system, this remarkable similarity must be accounted for in theories of solar system origin and evolution.

The Galileo spacecraft's telecommunication system was limited by the loss of a high-gain antenna that failed to unfurl before arrival at Jupiter (3). During the Io flyby, radio signals in the S band (2.3 GHz or 13-cm wavelength) were transmitted to Earth by a low-gain antenna with a temperature-controlled crystal oscillator (USO) (3) for frequency reference. The Deep Space Network (DSN) compensated for the low signal-to-noise ratio by tracking the spacecraft with their 70-m antennas in California, Australia, and Spain. They generated radio Doppler data from the carrier

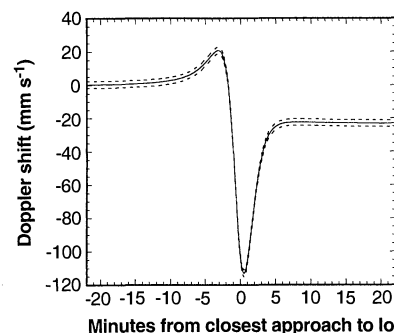


Fig. 1. Plot of the C_{22} Io gravity signal (solid line) detected in the USO Doppler data near the closest approach to Io. Doppler frequency shift is plotted according to the formula $c\Delta\nu/\nu$, where $\Delta\nu$ is the Doppler frequency shift in hertz, ν is the spacecraft's S-band transmitter frequency, and the speed of light $c = 2.998 \times 10^{11} \text{ mm s}^{-1}$. The dashed lines represent the $\pm 2 \text{ mm s}^{-1}$ standard error of the data.

J. D. Anderson and W. L. Sjogren, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099, USA.
G. Schubert, Department of Earth and Space Sciences, Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA.