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concentrations and temperature, and arrive at the unexpected conclusion that Eq. 2, and especially the heuristic crossover form Eq. 3, provide an excellent description of our data.

References and Notes
8. D. Stauffer, A. Aharony, Introduction to Percolation Theory, Revised 2nd Ed. (Taylor and Francis, Bristol, PA, 1994).

Micro/Nano Encapsulation via Electrified Coaxial Liquid Jets
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We report a method to generate steady coaxial jets of immiscible liquids with diameters in the range of micrometer/nanometer size. This compound jet is generated by the action of electro-hydrodynamic (EHD) forces with a diameter that ranges from tens of nanometers to tens of micrometers. The eventual jet breakup results in an aerosol of monodisperse compound droplets with the outer liquid surrounding or encapsulating the inner one. Following this approach, we have produced monodisperse capsules with diameters varying between 10 and 0.15 micrometers, depending on the running parameters.

Production and control of droplets and particles of micrometer or even nanometer size with a narrow size distribution are of interest for many applications in science and technology. Usually, these particles are formed as either an aerosol or a hydrocolloid phase. Aerosols and hydrosols of compound particles, such that each particle is made of a small amount of a certain substance surrounded by another one, are of particular importance for encapsulation of food additives (1–3), targetted drug delivery (4–10), and special material processing (11, 12), among other technological fields. All of them resort to encapsulation to provide such compound particles in the appropriate size range.

The interest in encapsulation may be motivated by a broad spectrum of reasons: to isolate an unstable component from an aggressive environment, to avoid decomposion of a labile compound under a certain atmosphere, to deliver a given substance to a particular receptor, and so forth. Although the substance to be encapsulated may be either solid or liquid, the encapsulating agent is usually a polymer carrying solution or a melted polymer. The key issue is the way to form the micrometer/nanometer-sized capsules from the bulk components, with controllable and adjustable coating thickness.

One of the most widely adopted methods to obtain micrometer/nanometer capsules is based on emulsion technology (13–15). Two immiscible fluids, one carrying the substance to be encapsulated and the other one carrying the polymer for the shell, are stirred to form an emulsion. This emulsion is stabilized by pouring it into a third solution (double emulsion process; DE), thereby extracting the polymer solvent and solidifying the polymer as a capsule. Related methods also incorporate phase separation and similar physical or chemical phenomena (16, 17).

Other approaches for encapsulation resort to the formation and control of liquid jets with diameters in the micrometer/nanometer range. In the electrospray (ES) technique, a conducting liquid is slowly injected through an electrified capillary tube. When the electric potential between the liquid and its surroundings rises to a few kilovolts, the meniscus at the tube exit develops a conical shape, commonly referred to as the Taylor cone. A thin microthread of liquid is issued from the point of the Taylor cone, which eventually fragments to form a spray of highly charged droplets (18). Its most well-known application has been in mass spectrometry, where it has been successfully exploited as a way to produce multiply charged gas phase ions of huge biomolecules present in the liquid phase (19). Another outstanding feature of the electrospray is its ability to generate monodisperse droplets whose size can be varied between hundred of micrometers and tens of nanometers, independent of the diameter of the capillary tube (20, 21).

In the simplest version of selective withdrawal (SW), the exit of a tube is located at a height 5 above the interface separating two immiscible liquids (or liquid gas). For low rates of fluid withdrawal Q, only the upper fluid is sucked through the tube. A sufficient increase in Q, or decrease in S, gives rise to a thin spout of the lower liquid surrounded by the outer fluid (22–24).

In the flow focusing (FF) technique (25, 26), a liquid is injected through a capillary tube whose exit is located close to a small hole drilled in a thin plate. A stream of another fluid (gas or liquid) surrounding the tube is forced through the hole. The mechan-
tical stresses exerted by this stream deform the meniscus attached to the tube exit. Then, the meniscus develops a cusplike shape from whose vertex a thin jet is issued. As in the electrospraying case, the jet diameter is also independent of the much larger diameter of the capillary tube.

In the DE methods, the capsules consist of a polymer matrix in which the encapsulated substance is somehow randomly distributed in tiny packets. The mean size of the capsules may vary between hundreds of nanometers and hundreds of micrometers, whereas the dispersion in sizes presents a relatively high standard deviation (usually larger than 100%).

Although each of these methods is able to produce encapsulated particles with a well-defined size range, good control over the thickness of the coating, or a specific size of coated particle, they are unable to accomplish all three of the desired parameters.

We report a technique that uses electrohydrodynamic (EHD) forces to generate coaxial jets of immiscible liquids with diameters in the nanometer range (27). The spray generated from the varicose breakup of the jet consists of monodisperse compound droplets, which can reach sizes well below the micrometer range. The basic experimental setup for the technique is sketched in Fig. 1. Two immiscible liquids, red and blue, are injected at appropriate flow rates through two concentrically located needles. The inner diameter of the inner needle ranges from the order of 1 mm to tens of micrometers, whereas its outer diameter sets limits to the cross section of the outer needle. The outer needle is connected to an electrical potential of several kilovolts relative to a ground electrode (the extractor). The inner needle is kept to an electrical potential that, depending on the conductivity of the outer liquid, can be varied from that of the outer needle to that of the extractor. For a certain range of values of the electrical potential and flow rates (28), a structured Taylor cone is formed at the exit of the needles with an outer meniscus surrounding the inner one (see Fig. 2A). A liquid thread is issued from the vertex of each one of the two menisci, giving rise to a compound jet of two coflowing liquids (see Fig. 2B). At the minimum jet section, the two-layered jet shown in Fig. 2B has an outer diameter of 4 μm.

In the case of the experiment in Fig. 2, A and B, the outer liquid was DuPont photopolymer Somos 6120, and the inner one was colored ethylene glycol (EG). To develop this structure, we injected Somos, which flowed through the annular gap between the two needles. We then increased the electrical potential of the outer needle $V_s$ until the liquid meniscus jumped into a stable cone-jet mode. In this particular example, the electrical potential of the inner needle was maintained at $V_s = V_i$. The viscosity of the outer liquid is sufficiently high to diffuse the electrical stressing acting on the surface into the bulk. Consequently, the liquid motion inside the Taylor cone is dominated by viscosity, so that the liquid velocity inside the cone is everywhere pointing toward the cone apex (29). The second liquid flowed through the inner needle to form a new meniscus inside the Somos one. The motion of Somos deformed the EG meniscus to a conical shape and sucked it from the meniscus’s tip to form a thin microthread. This microthread of EG merged with that of Somos at the tip of the Taylor cone to finally form a two-concentric layered micro/nano jet.

To obtain a structured Taylor cone, the EHD forces must act on at least one liquid, although they may act on both. We shall call the driving liquid the one upon which the EHD forces act to form the Taylor cone. We introduced a configuration in which the driving liquid flows through the needle’s annular gap (see Fig. 1). However, there is an alternative configuration in which the driving liquid flows through T2, whereas the second one flows through the annular gap between T1 and T2. That is the case shown in Fig. 2, C and D, where a Taylor cone of water is formed inside a meniscus of a nonconductive liquid such as olive oil. The electrical stresses acting on the charged water–olive oil interface, which are efficiently transmitted by viscosity toward the olive oil bulk, set the olive oil into motion, toward the water cone vertex. These two coflowing streams eventually give rise to a coaxial jet of water coated by olive oil. As in regular electrosprays, the motion of the driving liquid in this second configuration does not need to be dominated by viscosity. Olive oil (or any other liquid insulator) cannot be electrosprayed on its own in the cone-jet mode, because the lack of surface charge density prevents the formation of a steady Taylor cone (30).

The stability of the structured Taylor cones and the electrified compound jets strongly depends on the physical properties of the working fluids as well as the liquid flow rates and applied voltages. This complex electro-fluid-mechanical scenario is rather poorly understood, so that the stability domains for most liquid couples remain to be investigated. In the absence of better knowledge, we should point out that stable structured Taylor cones have been obtained for liquids satisfying the condition $\sigma_i > \sigma_o$, where $\sigma$ is the liquid-dielectric atmosphere surface tension and subscripts i and o refer to the inner and outer liquid, respectively.

Experiments show that the scaling laws (electrical current and droplet diameter as a function of flow rate) that govern regular electrosprays (20, 31, 32) also apply to these compound electrosprays. In this situation, the flow rate must be that of the driving liquid. For example, data in Fig. 3A, obtained by electrospraying water coated with oil, show a

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**Fig. 1.** Typical experimental setup for a structured Taylor cone.

**Fig. 2.** (A) Structured Taylor cone and (B) downstream detail of the two coaxial jets emitted from the vertex of the two menisci. A Taylor cone of water coated by (C) a thin shell of olive oil and by (D) a thick shell of olive oil.
remarkable agreement with the well-known $I \sim Q^{1.5}$ law, where $I$ is the current and the flow rate $Q = Q_{\text{in}}$ is, in this case, that of water (the driving liquid). Furthermore, as shown in Fig. 3B, the value of the current is not substantially affected by changes on the oil flow rate, as far as both flow rates are comparable.

This behavior as regular electrospays is expected because, from the electrical point of view, the role played by the olive oil (insulator) is exactly that played by air in regular electrospays. The oil reduces the intensity of the electric field felt by the driving liquid (water) by a factor proportional to its dielectric constant, but, as with air, it makes no contribution to the net charge transport. Nonetheless, for much lower values of the oil flow rate, strong variations of $I$ with $Q_{\text{out}}$ have been found.

We applied this technique to microencapsulate aqueous solutions. An outer jet of nonvolatile olive oil must surround them. The hardening process can also be thermally or chemically initiated under the use of appropriate reagents.

In Fig. 3A, we show the differential mobility spectra recorded from an electrospray of a NaCl aqueous solution. The liquid flow rate through the electrospray was 18 nl s$^{-1}$. The scale on the horizontal axis is proportional to $Z/V$, where $Z$ is the electrical mobility in cm$^2$ V$^{-1}$ s$^{-1}$, and $V$ is the initial voltage. The leftmost peak is due to ions of sodium (Na$^+$) at different solvation states. The peak in the middle is mostly due to clusters of salt plus sodium ions at different states of charge and solvation. The third peak is due to the solid residues left after solvent evaporation from the droplets. Because the initially electrosprayed droplets evaporate and undergo Coulombic explosions, the sizes of the solid residues bear little relation to the initial droplet size, if any at all. The peaks associated with ions and ionic clusters have completely disappeared. There is only a single dominant peak, associated to the monodisperse electrospay compound droplets. Indeed, the size of such droplets, as inferred from the measured electric current and the liquid flow rate emitted from the electrospay, scales as those predicted by electrospay laws. The absence of ionic species and Coulomb explosions, together with the matching of predictions in size and charge, strongly supports the picture that the water droplets do not evaporate, so a thin shell of nonvolatile olive oil must surround them.

Encapsulation, tested within the nanometer range, has been carried out via aerosol techniques, because they allow for on-line characterization of the airborne particles. In particular, we resorted to mobility analysis with a differential mobility analyzer (DMA) described elsewhere (33). Electrospay droplets, when subjected to sufficient liquid evaporation, lead to the formation of gas phase ions of substances previously dissolved in the liquid (34, 35), as in the case of aqueous solutions of salts.

In Fig. 5A, we show the differential mobility spectra recorded from an aqueous solution of NaCl. The liquid flow rate through the electrospray was 18 nl s$^{-1}$. The scale on the horizontal axis is proportional to $Z/V$, where $Z$ is the electrical mobility in cm$^2$ V$^{-1}$ s$^{-1}$. The leftmost peak is due to ions of sodium (Na$^+$) at different solvation states. The peak in the middle is mostly due to clusters of salt plus sodium ions at different states of charge and solvation. The peak in the middle is mostly due to clusters of salt plus sodium ions at different states of charge and solvation. The third peak is due to the solid residues left after solvent evaporation from the droplets. Because the initially electrosprayed droplets evaporate and undergo Coulombic explosions, the sizes of the solid residues bear little relation to the initial droplet size, if any at all. In Fig. 5B, we show the differential mobility spectra gathered from the same aqueous solution, flowing at the same rate, but with 27% (in flow rate) of nonvolatile olive oil coflowing on the outside. The result is markedly different. The peaks associated with ions and ionic clusters have completely disappeared. There is only a single dominant peak, associated to the monodisperse electrospay compound droplets. Indeed, the size of such droplets, as inferred from the measured electric current and the liquid flow rate emitted from the electrospray, scales as those predicted by electrospay laws. Thus, the absence of ionic species and Coulomb explosions, together with the matching of predictions in size and charge, strongly supports the picture that the water droplets do not evaporate, so a thin shell of nonvolatile olive oil must surround them.

Figure 6 shows the diameter of the capsules generated from structured jets of olive oil (outer fluid) and water solutions (inner

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**Fig. 3.** (A) Current $I$ as a function of the water flow rate $Q_{\text{in}}$ for a given value of the oil flow rate $Q_{\text{out}}$. (B) Plot showing the independence of the current from $Q_{\text{out}}$.

**Fig. 4.** Collection of near monodisperse capsules. Magnified views of two capsules formed under different parametrical conditions are also given in the figure. In (A), the outer diameter is 10 \( \mu \text{m} \), whereas the diameter of the capsule shown in (B) is 8 \( \mu \text{m} \). The hardening process can also be thermally or chemically initiated under the use of appropriate reagents.

**Fig. 5.** Differential mobility spectra of (A) electrospays of water solutions and (B) a compound electrospay of the same water solutions (inner) and olive oil (outer).

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**Fig. 6.** The diameter of the capsules.
R E P O R T S

Fig. 6. Typical sizes of capsules of water surrounded by a thin shell of olive oil. □, $Q_w = 39.8e-12 \text{ m}^2 \text{s}^{-1}$; ▲, $Q_w = 26.0e-12 \text{ m}^2 \text{s}^{-1}$; ◇, $Q_w = 18.4e-12 \text{ m}^2 \text{s}^{-1}$; ; $Q_w = 17.8e-12 \text{ m}^2 \text{s}^{-1}$; △, $Q_w = 25.5e-12 \text{ m}^2 \text{s}^{-1}$; and □, $Q_w = 15.6e-12 \text{ m}^2 \text{s}^{-1}$.

A Thermally Re-mendable Cross-Linked Polymeric Material

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We have developed a transparent organic polymeric material that can repeatedly mend or “re-mend” itself under mild conditions. The material is a tough solid at room temperature and below with mechanical properties equaling those of commercial epoxy resins. At temperatures above 120°C, approximately 30% (as determined by solid-state nuclear magnetic resonance spectroscopy) of “intermonomer” linkages disconnect but then reconnect upon cooling. This process is fully reversible and can be used to restore a fractured part of the polymer multiple times, and it does not require additional ingredients such as a catalyst, additional monomer, or special surface treatment of the fractured interface.

In past decades, highly cross-linked polymers have been studied widely as matrices for composites, foamed structures, structural adhesives, insulators for electronic packaging, etc. (1, 2). The densely cross-linked structures are the basis of superior mechanical properties such as high modulus, high fracture strength, and solvent resistance. However, these materials are irreversibly damaged by high stresses (3, 4) due to the formation and propagation of cracks. The latter lead to dangerous loss in the load-carrying capacity of poly-