

# Behavior of fluids in nanoscopic space

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Geometry plays a fundamental role in the evolution of a class of nonequilibrium systems called cellular structures (1). The evolution of stable cellular structures is characterized by universal or system-independent statistical distributions, which possess scaling properties. These systems play important roles in various technological applications. The uses of foams range from transport of granular media in pipes to fire suppression and explosion attenuation (2). Polycrystalline thin films are used in electronic devices such as MOSFET transistors (3), magnetic storage media (4), and conductors (5). The technological performance of these materials depends on the characteristics of their inherent cellular structure. For example, the strength of a polycrystalline metal under stress depends on the average grain size (6). The phenomenon of electromigration, which occurs along grain boundaries in thin film conductors, is responsible for their electronic noise and eventual failure. Mean times to failure have been shown to depend on mean grain size (7) and, surprisingly, on grain geometry (8). Controlled cellular structure formation in novel materials is, however, inherently interesting. The work by Chakrapani *et al.* (9) in a recent issue of PNAS demonstrated the formation of cellular structures out of vertical carbon nanotube arrays on silicon that can be floated off the substrate.

Carbon, besides being the basis of all living matter, contributes some of the most extraordinary properties to artificial materials. For example, a ring of  $n$  odd-numbered  $sp^2$  bonded carbon atoms would be an insulator when  $n$  is small, say 5, 7; a metal when  $n$  is large,  $>13$ ; and a semiconductor for intermediate numbers (10). These  $[2n]$ trannulenes still remain “theoretically interesting” molecules, but their cylindrical homologues, carbon nanotubes (CNT) (Fig. 1), have been synthesized as either concentric cylinders called multiwalled carbon nanotubes (MWNT) (11) or single cylinders called single-walled carbon nanotubes (SWNT) (12, 13). Widely recognized as the quintessential nanomaterial (14), carbon nanotubes are recognized as the ultimate carbon fiber with the highest strength of any material (15, 16) and the highest thermal conductivity (17), and they have been shown to pos-

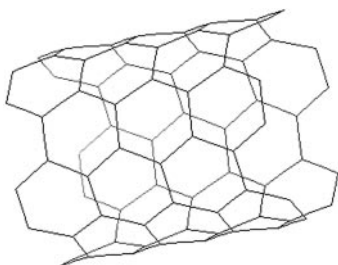


Fig. 1. Schematic structure of a single-walled carbon nanotube.

sess outstanding field emission properties (18). The metallic carbon nanotubes transport electric current ballistically (they do not dissipate heat) (19). They can also function as the active semiconductor in nanoscale devices (20), all as a result of their unique topologically controlled electronic properties (21).

Under suitable conditions, MWNTs can be grown vertically in periodic arrays (Fig. 2) on various substrates (22). The length and diameter of the nanotubes can be controlled (23). The covalently bonded carbon structure gives rise to the high strength of the material and provides an extremely hydrophobic surface. Most commonly, chemical processing of CNTs is carried out with the goal of overcoming the hydrophobicity

## Water confined within internanotube hydrophobic channels can form a system of independent mathematical networks.

of the surface, to render the material compatible with solution state manipulations (24–26). Thus, the work of Chakrapani *et al.* (9) shows for the first time a radical shift in emphasis: that the behavior of water and other polar solvents, confined within the internanotube hydrophobic channels, can be controlled to form a system of independent mathematical networks.

The oxidation of the nanotubes in the arrays by using the oxygen plasma is

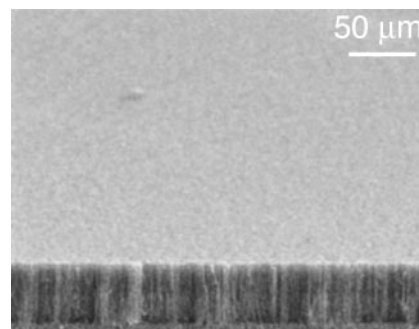


Fig. 2. Vertically aligned growth of carbon nanotubes on Si. Adapted from figure 1 of ref. 9.

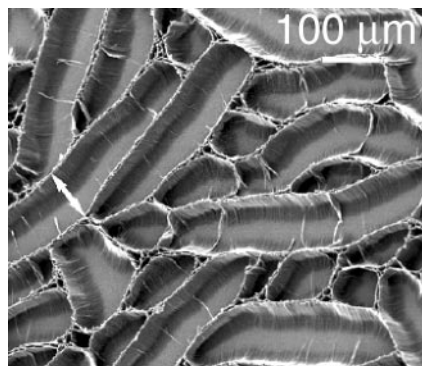
assumed to result in the removal of amorphous carbonaceous materials and perhaps an oxidation of the tip of the nanotubes without affecting the integrity of the side walls. This chemical modification would create a hydrophilic environment at the top surface with a hydrophobic inner nanoscopic cavity. The solvent molecules trapped within nanoscopic space can form thin sheets, where the transport properties are highly collective. As a result, the entire sheet can slip back and forth under thermal agitation (27). Thus, when water was allowed to evaporate slowly, the capillary action of the nanotube channels forced them to collapse and the motion of the water sheet gave rise to the grain boundaries. It was observed that freeze-drying of the wet nanotube membranes did not form the cellular structures, thus showing that the motion of the solvent sheets was necessary to form the boundaries.

The observed formation of the polygonal structures (Fig. 3), in contrast to crack patterns that are terminated by preexisting cracks, indicates that the energy associated with the edges influences the topological properties of the edge network. The system tends to minimize its total energy by minimizing the total length of the edge network. It can do so only in a way compatible with local connectivity constraints as best illustrated by considering four points on the plane that one is asked to join by lines, so that the overall length of the latter is

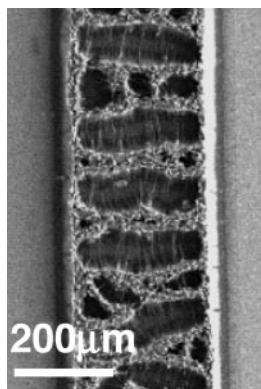
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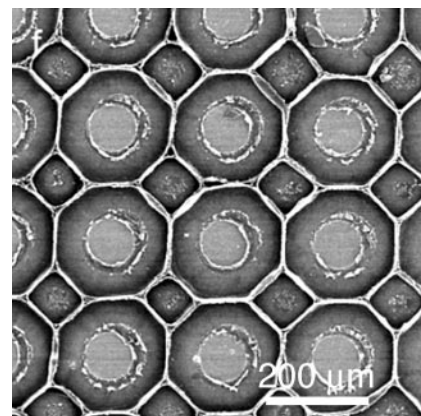
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**Fig. 3.** Topology of cellular structure formed from carbon nanotubes on Si. Adapted from figure 1 of ref. 9.



**Fig. 4.** Alignment of the cells within a column of carbon nanotube array. Adapted from figure 4 of ref. 9.



**Fig. 5.** Cellular pattern formed by solvent migration through the nanoscopic pores in a carbon nanotube array. Adapted from figure 4 of ref. 9.

minimal. The rate of change of area of a cell thus formed to the number of its sides can be related by the von Neumann theorem. It governs the continuous evolution that drives a cellular structure toward topological changes and consequently to changes in the average characteristic scale (1). That the cells form independent of each other and continuously evolve to minimize energy is supported by the observation of multiple layers of the boundaries. Further, it was established that the average cell width changes inversely with the rate of evaporation of the solvent.

The observed alignment of the nanotubes at the cell boundaries is remarkable (Fig. 3). It indicates that the boundary formation process does not involve any exchange of water from within the membrane, during the evaporation process. This confinement would

give rise to a membrane potential, much like in biological cells (27). Further shrinking the internanotube space from 50 nm to 1 nm (28) would give rise to cellular structures controlled by the molecular properties of water. It is well known that in biological cells, the structure of water confined in nanoscopic space is very different from that in the bulk. The observation of the cell alignment in nanotubes grown on varying widths (Fig. 4) also indicates that the solvent enters the nanotube array only from the top, hydrophilic surface, thus leaving the side walls intact.

Finally, when the solvent was compartmentalized within a nanotube array (Fig. 5), the evolved structure was very similar to that simulated for the time averaged osmotically driven flow of water through semipermeable membranes

of CNTs (29). Clearly, the solvent “slip” along the hydrophobic pore walls of the CNTs is controlled by fluid–wall interactions. Such slip-flow behavior can be vital for generating the high-throughput rates required in nanofluidic devices (27, 30).

Further refinement of the observed phenomenon can lead to the synthesis of living membranes, where concentration gradients will govern the directionality and flow of fluids. The observation of the cellular structures in this case was facilitated by the alignment and pinning of the nanotubes to the substrate, thus partially restricting two degrees of freedom. It is intriguing to consider the reverse situation, where the motion of nanoscopically confined fluids is allowed to reorganize a bulk anisotropic sample of carbon nanotubes.

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