ROBOTICS WITH COLLOIDAL AUTONOMOUS SYSTEMS

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ABSTRACT

Organic, inorganic or hybrid liquid devices enable morphing capabilities in response to external stimuli; such biologically inspired systems could be protected by the external environment, such as a planetary atmosphere, by a flexible skin. Their reaction to a command could also be an internal reconfiguration, such as an order / disorder transition, or a transition between two different order states. Our paper provides an assessment of existing technologies that could be used to create a "Smart Fluid System" or a "Colloidal Autonomous Systems".

1. COLLOIDAL ROBOTICS

Compared to conventional robotic systems (i.e., anything not liquid), colloid-based robotic systems offer enormous promises, in terms of versatility, adaptability, resiliency, distributed architecture, and autonomy, but have not yet been investigated. A soft and deformable robot is a desirable platform for adapting to unpredictable terrain, navigating through small holes, or even for interacting with humans where unintentional infliction of harm is of great concern. This brings along future applications in the exploration of harsh environments, for example gas giant planets or small bodies like comets and asteroids, oceans and lakes depths, rough terrains, post-earthquake areas, surgery, and so on. The scope of this paper is to report on the ad state-of-the-art of materials science and robotic systems technology in the field of Smart Fluid Systems (SFS) / Colloidal Autonomous Systems (CAS) that will lead to the research and technology development of liquid robotic systems in the near future.

2. DEFINITIONS

- **Liquid** is a condensed matter state, having no shape retention but an almost perfect volume retention, as a consequence of a pressure variation.
- **Colloid** is a complex condensed matter system lying at the boundary between totally homogeneous systems (solutions) and totally heterogeneous systems (suspensions). They can be classified according to the aggregation state of their constituents (S=solid, L=liquid, G=gaseous): S-S (solid sol), S-L (solid emulsion), S-G (solid foam / aerogel), L-S (sol), L-L (emulsion), L-G (liquid foam), G-S (solid aerosol), G-L (liquid aerosol), G-G, where the first letter refers to the dispersant (carrier phase) and the second to the dispersoid (suspended phase). Typically colloids have peculiar properties that cannot be explained by superposition of single constituents properties.
- **Filler** or **dispersoid** is a solid (nano- or micro-) particle of different chemophysical nature with respect to the carrier solvent.
- **Ferrofluid** (**FF**) is a colloidal suspension of magnetic NPs (nanoparticles) where long-range attractive interactions occur, compensated by short range repulsive ones.
- **Magneto(electro)rheological fluid** (**M(E)RF**) is an unstable liquid phase, a ferromagnetic(dielectric) suspension that could be stabilized by the external application of a magnetic(electric) field and formed as a result of magnetization(polarization) forces.

3. MATERIALS AND SUBSYSTEMS

Typically an autonomous robotic system should be able to: locally store / generate / harvest energy, and convert it in a suitable form easy to distribute to the internal subsystems; sense / measure at least one physical parameter; distribute information internally, transmit it externally, store it and make computations; move. A plethora of different materials at the liquid state could be used to achieve such functionalities, as we will discuss in the following subsections.

3.1. Energy subsystems

First of all we will discuss possible energy generation subsystems. The bottom-up construction of artificial organelles to distribute bioenergy has been pointed out (Figure 1a). [1] The synthesis of adenosine or guanosine triphosphate (ATP or GTP), accomplished by photoactivated enzymes dispersed in the synthetic cytoplasm of a SFS, could achieve quantum yields as high as 7% (Figure 1b). [2] Enzymes have the drawback of pressure and temperature ranges to be kept under control, to avoid denaturation. Researchers achieved an ATP synthesis efficiency of 4 ng/min/mg of ATP synthase. ATP molecules could diffuse into the liquid matrix of the SFS in a concentration driven process.

The photogeneration of a proton gradient across the

membrane of a synthetic protocell was recently reported, achieving an efficiency of 0.061 pH units per minute, equivalent to an electromotive force of 3.6 mVmin^{-1}, that could be harvested to produce ATP. [3]
Changing completely paradigm, FFs could act as thermal ratchets, when submitted to a particular configuration of DC and AC magnetic fields, (Figure 1c). [4, 5] Such subsystem could harvest thermal energy (Brownian motion) by suitably placed microcoils to collect induced electromotive forces.
ElectroChemical cells are at the basis of a current trend in neuromorphic electron devices, that would reversibly change impedance state based on a redox reaction. A thin film multilayered stack $Ag/SiO_2/Pt$ is such that Ag in the metallic state gets oxidized generating Ag^+ ions that react with OH^- available at the Pt electrode, creating a metallic Ag bridge across silica. The voltage controlled, perfectly reversible reaction induces electromotive forces and corresponds to a charge stored in the multilayered stack, according to an arrangement called nanobattery (Figure 1d). [6]
The typical charge that could be stored in a device having a typical vertical structure (30-50 nm of SiO_2, area of 2×10^{-4} cm^2) is ≈ 5 nC. Now shifting the paradigm from the thin film arrangement to the core-shell multilayered NPs, in order to have the same area one would need ≈ 300,000 particles. Calculating a maximum volume ratio of 5% of functional fillers with respect to the solvent, we would have a volume of about 1×10^{-14} cm^3, in other words 1 single cc of nanobattery-SFS could be potentially able to store 500,000 C! If we were able to efficiently collect such a huge charge, we would have volume energy densities of ≈ 180 Wh/l, higher than the standard lead-acid cell (up to 100 Wh/l) and comparable to NiCd rechargeable batteries (up to 200 Wh/l). Since the density of a SFS is quite close to that of water, the mass energy density of ≈ 160 Wh/kg seems perfectly comparable with that of Li-ion cells (up to 200 Wh/kg), with the additional advantage brought by the liquid state (Figure 1e). [7]

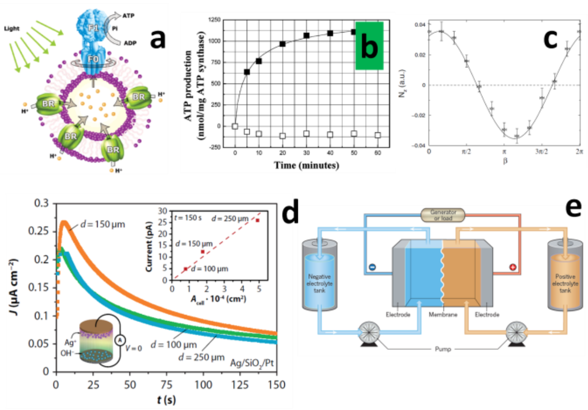

Figure 1. Energy generation / storage – enabling subsystems. A: Schematic representation of proteopolymersomes where ATP synthase (composed by the membrane-integrated domain Fo and the soluble domain F1) uses an electrochemical proton gradient generated by the energy transducing protein bacteriorhodopsin (BR) to synthesize ATP from ADP and inorganic phosphate (Pi). B: Photoinduced ATP synthesis in the BR-ATP synthase proteopolymersomes. The production per milligram of proteic complex is shown as a function of illumination time (full dots) and compared to dark reference (open dots). C: Magnetic torque transferred to a FF in an experimental setup as a function of the phase angle β of an AC magnetic field applied along y-axis plus a DC static magnetic field applied along x-axis, where macroscopic torque is generated by thermal noise and Brownian motion. D: short circuit current density measurement of a nanobattery based on a thin film stack $Ag/SiO_2/Pt$, showing discharge curves at different cell sizes. E: renewable liquid energy storage concept, where tanks of liquid metals or polymers represent positive and negative sides of a flow battery.

3.2. Sensing subsystems

FFs feature an extremely strong light scattering, that could be exploited for sensing purposes. In particular the Photonic Hall Effect (PHE) and the Optical Magnetoresistance effects (OMR) are of interest for practical applications. [8] PHE enables a highly accurate reading of the external magnetic field in a limited range. [9] The liquid sensor saturates above 0.1 T and features a quasi-linear response in the mT range (Figure 2 a, b). The Rayleigh – Taylor instability could be used to measure the gravitational field in the presence of a magnetic field, thanks to surface roughness waves that appear at the interface between FF and the external volume (Figure 2 e, f). [10]

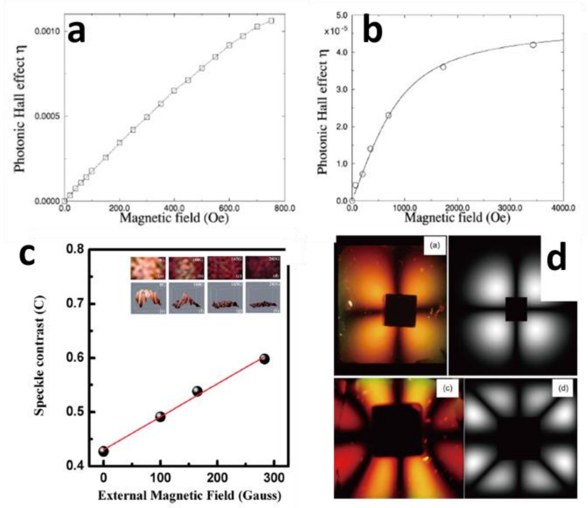

Figure 2. Sensing – enabling subsystems. A: Experimental measurement of the PHE generated by a sol-gel of cobalt ferrite at low magnetic fields, with a

frequency of 560 Hz. B: same as before in the high field regime and with a frequency of 40 Hz. C: linear variation of speckle contrast of backscattered speckles as a function of external magnetic field, induced by Raileigh – Taylor instabilities. D: forward scattered patterns of a FF for different magnetic field strenghts (in the inset the value in Gauss).

3.3. Information subsystems

When dealing with collective complex systems, the most advanced concept enabling information elaboration and storage is that of Resistive Switching Devices (RSDs), two terminal electron devices whose impedance state is changed by an electric potential and read (unchanged) through a resistivity measurement. RSDs have been reported to work down to 5K (Figure 3 a, b). [11] A possible implementation of RSDs is that of distributed NP-based computing, taking advantage of the liquid matrix and inherent rad-hard functionality. RSD functionality was reported by characterizing biological fluid living organisms, such as Physarum Polycephalum (Figure 3 c, d). [12] Also human blood behaves as a RSD. [13] Synthetic colloids have also been reported based on ZnO NPs dispersed in a liquid monomer. [14]

We have proposed the concept of Localized Colloidal Microantennas (LoCµAs), based on Metal-Like Liquid Films (MeLLFs), built on the surface of the SFS. MeLLFs are a stabilized layer of metallic NPs trapped at the interface between two immiscible liquids. [15, 16] When such particles feature a Plasmon resonance, the collective oscillations of their charge carriers (electrons) make them behave as an optical mirror, therefore a surface capable of emit and reflect electromagnetic waves. Small volumes of MeLLFs could be used to create liquid reflectors, with a typical diameter ranging from 100 µm to 10 cm.

LoCµAs could be adaptable and reconfigurable according to pressure waves sent in the synthetic cytoplasm by proper piezoelectric actuators.

FFs are extremely efficient microwave absorbers, as their absorbance was assessed up to 46 dB (99.9% attenuation) in the range 8-13 GHz (Figure 3 e, f). [17, 18] Regarding optical frequencies, ordered arrays of Co NPs in a FF, under the effect of a magnetic field, realize a tunable photonic hyper-crystal. [19]

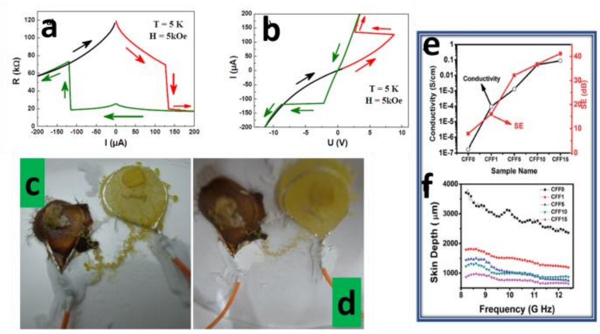

Figure 3. Information elaboration and storage – enabling subsystems. A: Resistance versus current of a nanocolumnar LSMO/Al_2O_3/LSMO device at 5 K. B: Extrapolated IV curve in the same system as before. C: Physarum Polycephalum inoculated with NPs before electrical characterization. D: same as before after electrical characterization, showing connection thinning and burning out of unnecessary connections. E: Conductivity and Shielding Efficiency (SE) of different liquid formulations containing reduced graphene oxide and FFs. F: skin depth measurements of the same formulations as a function of frequency in the GHz range.

3.4. Mobility subsystems

Hydrodynamic interaction promotes the emergence of collective motion in a colloidal system in the form of a macroscopic flow (Figure 4 a to c). [20] Propulsion was obtained consuming a chemical propellant, in an ionic liquid environment, moving a liquid metal volume for more than 45 m (Figure 4 d to i). [20] Optical guidance of NPs dispersed in a medium is also possible, using the so called optical trapping and exploiting the collective properties of magnetic elements. [21] The possible mechanisms to convert light into motion are: radiation pressure, optical tweezers, light induced wettability gradients, thermocapillary effect, photosensitive surfactants, chromocapillary effect (isothermal variation of surface tension, inducing a Marangoni flow), optoelectrowetting, photoelectroosmotic effect and optical dielectrophoresis (Figure 4 j). Peristaltic motion, popular in worm-like animals, could be exploited where the gravitational field allows achieving friction. [22] Varying the stiffness of small liquid volumes positioned on the surface of the outer skin of the SFS, filled by either MRF or ERF, is a possible solution.

Chains of self-assembled Janus ellipsoids can be elongated or contracted by 36 % exploiting electric fields, a very interesting solution for the mobility of SFS. [23]

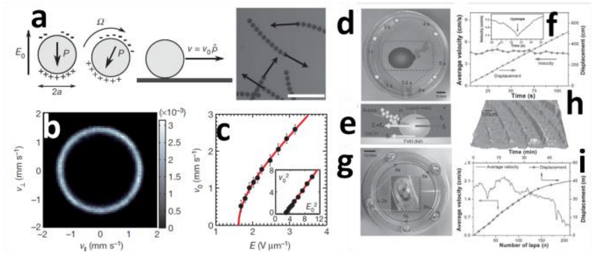

Figure 4. Mobility – enabling subsystems. A: Sketch of the Quincke rotation and self-propulsion mechanism of a colloidal roller characterized by its electric polarization P and superposition of ten successive snapshots of colloidal rollers in a time interval of 5.6 ms, scale bar 50 µm. B: Probability distribution function of the velocity vector for isolated rollers, where the parallel direction of velocity is that corresponding to the tangent of racetrack. C: Roller velocity plotted versus electrical field amplitude. D: self-fueled liquid metal motor based on EGaIn droplet of 60 µl volume running in a circular Petri dish containing 0.25 mol/L NaOH solution. E: schematics of forces affecting the velocity of the liquid motor. F: Time-average velocity and displacement in a 112 s observation window. G: 160 µl volume droplet running in a circular open-top channel. H: surface topography of the circular channel. I: lap-average velocity and time-displacement plots in a 1 h observation window.

4. CONCLUSIONS

We have introduced the concept of Smart Fluid Systems (SFS) / Colloidal Autonomous Systems (CAS), based on organic or inorganic colloids, contained inside a confining membrane that protects them from a harsh planetary environment. We have discussed their fundamental subsystems that could allow energy storage / generation, sensing, information storage / transmission / computation, and mobility. Such SFS would have the potential of offering innovative solutions to planetary exploration, in environments such as gas giants and asteroids / comets, where conventional robotic systems encounter many problems.

5. ACKNOWLEDGMENT

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