

FIELD INDUCED MICROPARTICLE STRUCTURE FORMATION IN FLUIDS

FORMACIÓN DE ESTRUCTURAS DE MICROPARTÍCULAS EN FLUIDOS INDUCIDAS POR CAMPO

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We review how magnetic and electric fields can be used to create microparticle structures within fluids such as water, oil, polymers, or ferrofluids. The particular arrangement of the electrodes will strongly influence the morphology of the clusters or networks formed, as will also rotating or oscillating fields do. The structure and dynamics of such pattern formation will be described for various types of particles, such as colloidal microspheres, carbon nanoparticles, and metal particles.

Revisamos cómo los campos eléctricos y magnéticos pueden utilizarse para crear estructuras a partir de micropartículas en fluidos como agua, aceite, polímeros o ferrofluidos. El arreglo de electrodos utilizado influye poderosamente la morfología de los “clusters” en las redes que se forman, como también lo hacen los campos rotatorios u oscilatorios. Se describen la estructura y dinámica de la formación de éstos patrones para varios tipos de partículas, tales como microesferas coloidales, nanopartículas de carbono, y partículas metálicas.

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INTRODUCTION

Formation of aligned structures within fluids can be obtained by a range of techniques. It is known that mechanical shear in a flowing fluid can align nanoparticles in the fluid into linear chain-like structures [1]. Allowing the fluid to pass above a surface containing protruding micro- or nanostructures leads to similar effects. Static (DC) or oscillating (AC) electric fields may be employed to assemble and align uncharged dielectric particles. Similarly, relatively weak magnetic fields may be used to align dia- or paramagnetic particles.

The motion of charge-neutral particles in a fluid induced by inhomogeneous electric field (AC or DC) is called dielectrophoresis [1]. Magnetophoresis is the similar effect of motion of dia-/paramagnetic particles induced by inhomogeneous magnetic fields [1]. In these two processes a single particle will first be polarized (electrically or magnetically) by the difference in the dielectric constant or the magnetic permeability between the particle and its surrounding carrier fluid. This induced dipole is then pushed away from or attracted toward the source of the field by the field gradient. If another similar particle is placed in the neighborhood of the first, they interact with dipolar forces and will be attracted or repelled depending on the angle between a vector \mathbf{r}_{ij} joining their centers and the direction of the external field. Thus, spherical microparticles in an external field interact via the dipolar potential

$$U \propto \sum_{i \neq j} \frac{1}{r_{ij}^3} \left[\sigma_i \cdot \sigma_j - 3(\sigma_i \cdot \mathbf{u}_{ij})(\sigma_j \cdot \mathbf{u}_{ij}) \right], \quad (1)$$

where σ_n is the electric dipole moment \mathbf{p}_n , or the magnetic moment \mathbf{m}_n , of the n -th particle, see Table 1. Here, \mathbf{u}_{ij} is a unit vector in the direction of \mathbf{r}_{ij} . In addition, any gradient in the external E - or H -field gives rise to a single particle force with a direction that depends only on the difference $\varepsilon_2 - \varepsilon_1$ of the dielectric constants, or $\mu_2 - \mu_1$ of the permeabilities, of the particles and the fluid, respectively. This is outlined in Table 1.

MICROPARTICLE ALIGNMENT IN FLUIDS

Figures 1 (a) and 1 (b) show some examples of dielectrophoretic alignment of microparticles using AC electric fields. Figure 1 (c) shows chain formation of magnetic particles in water in a very weak magnetic field [2] and Fig. 1 (d) shows alignment of nonmagnetic polystyrene spheres dispersed in a ferrofluid [3] in a constant magnetic field $H \approx 800$ A/m [4]. The growth dynamics of such chains follow the cluster-cluster aggregation model [5] where the typical cluster length L grows with time t as $L(t) \sim t^z$ with $z \approx 0.5$ [6]. Also, the distribution of cluster sizes at different times can be rescaled to a common, “universal” functional form [4]. Using an in-plane rotating magnetic field circularly shaped aggregates can be obtained instead of linear strings [7]. Similar structures have been found in experiments

Table I Electric and magnetic force expressions		
External E -field Force on electric dipole p	$F_{edip} = (p \cdot \nabla) E_0$	
Dipole moment of sphere with radius a inside fluid	$p = 4\pi\epsilon_1 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} \right) a^3 E_0$	Dielectric constants: ϵ_1 for fluid ϵ_2 for particles
Dielectrophoretic force on spherical particle	$F_{DEP} = 2\pi\epsilon_1 K(\epsilon_1, \epsilon_2) a^3 \nabla (E_0^2)$	$K(\epsilon_1, \epsilon_2) = \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} \right)$ Clausius-Mosotti factor
External H -field Force on magnetic dipole m	$F_{mdip} = \mu_0 (m \cdot \nabla) H_0$	
Magnetic moment of sphere inside fluid	$m = 4\pi\mu_1 \left(\frac{\mu_2 - \mu_1}{\mu_2 + 2\mu_1} \right) a^3 H_0$	Magnetic permeabilities: μ_1 for fluid μ_2 for particles
Magnetophoretic force on spherical particle	$F_{MAP} = 2\pi\mu_1 K(\mu_1, \mu_2) a^3 \nabla (H_0^2)$	$K(\mu_1, \mu_2) =$ magnetic Clausius-Mosotti factor

and computer simulations of soft magnetic microparticles in uniaxial and biaxial magnetic fields [8] and 3-D networks of strings inside composites have been found using triaxial magnetic fields [9].

PARTICLE ALIGNMENT FOR CONDUCTIVE COMPOSITES

Field-assisted microparticle alignment in polymer dispersions is a convenient and efficient way to create conductive composites with very low loading of conductive fillers. Typical schemes to do this is shown in Fig. 2. A very low volume fraction of conductive nano- or microparticles, such as carbon black (CB), carbon nano-disks and cones (CNC), graphite or metal particles, is dispersed in the polymer and made into a thin (10 – 100 μm) layer on top of a pair of in-plane metal electrodes as shown in Fig. 2 (a) - (c) [10, 11, 12]. The electrodes may be electrically insulated from the polymer dispersion using a plastic foil. Then, an AC voltage is applied between the electrodes and after a few seconds to about a minute, the conductive particles are assembled and aligned into chains by the electric field. These chains may span the gap between the electrodes, thus making a conductive channel in the polymer matrix. The field may alternatively be applied between a bottom

and a top electrode giving rise to conductive chains from one side of the layer to the other, Fig. 2 (d). The polymer can then be cured by heat or UV-light and the conductive chains are locked in place. Finally, the electrodes may be detached from the electrodes (Fig. 2 (c)), creating a free-standing film that is conductive either in-plane or perpendicular to the sheet.

The growth speed depends on the E -field strength and particle concentration as well as the configuration and separation of the electrodes [13]. Typical concentration of filler particles in these conductive films are 0.2 – 1.0 vol-%. This is well below the isotropic percolation limit for conductivity in such mixtures which is typically 2 – 5 vol-%. During the alignment, the electrical conductivity of the material rises from the conductivity of the pure polymer $\sim 10^{-6}$ S/m up to 10^{-3} – 10 S/m, depending on the type of filler particle. This conductivity increase takes place during the first minute of alignment and after that there is only a smaller increase as the chains reach their optimal configuration [11, 12]. Some type of chain rearrangement such as merging of two nearby chains and formation of “branched roots” at the electrodes may be seen but this has only a minor influence on the conductivity. After curing of the polymer the conductivity remains fixed. Figure 3 (a) and (b) show the cross section of a sample containing

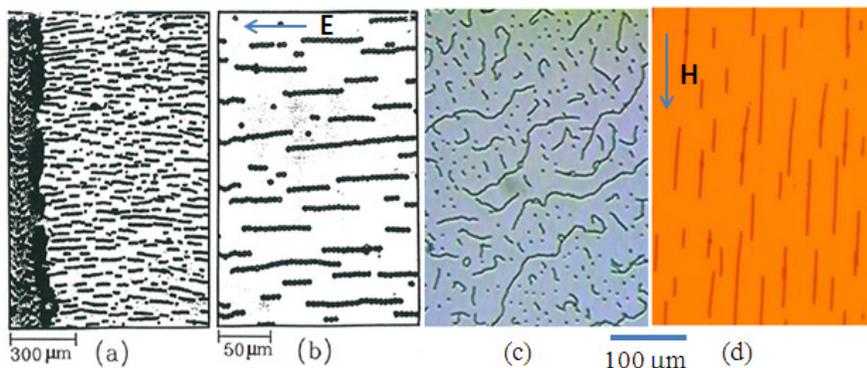


Figure 1: (a) and (b) Electric alignment of 5 μm polystyrene spheres in water at field frequency $f = 1$ kHz and $E = 5$ V/mm. (c) Permanent magnetic microbeads in a very weak in-plane magnetic field. (d) Alignment of 4 μm polystyrene microspheres in a ferrofluid.

0.2 vol-% CNC with field perpendicular to the layer (Fig. 2 (d)) before and after the alignment process [11].

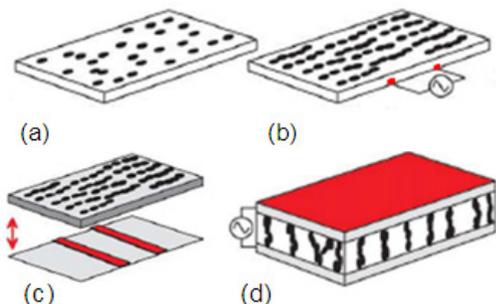


Figure 2: Alignment of particles in thin layers into conductive strings.

An array of electrodes with length 2 cm and spacing 100 μm and a field with frequency $f = 1 \text{ kHz}$ and strength $E = 200 \text{ V/mm}$ were used to produce the in-plane CNC channels seen in Fig. 3 (c) [10]. Using two needle-shaped gold electrodes on top of a 250 μm thick silicon substrate, the single CB string seen in Fig. 3 (d) was formed in about 100 s in an AC field with $E = 300 \text{ V/mm}$ [14, 15]. After UV curing, the substrate was bent slightly, resulting in a reversible resistivity change of the string by about 15%. Such strings may be used as strain sensors. No such change was detectable in a similar, isotropically filled sample containing 12 vol-% CB. Thus, the piezoresistivity is an effect of the particle alignment. Similar field-structured composites using magnetic fields and Au-coated Ni particles in epoxy have been studied by Martin *et al.* [16]. Such composites may have interesting thermoresistive, piezoresistive, and chemiresistive properties.

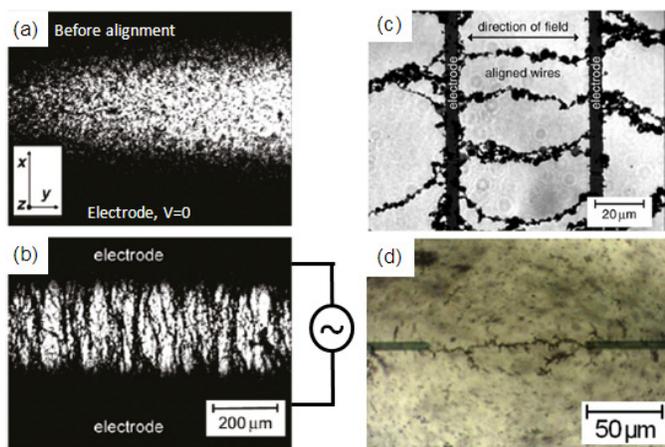


Figure 3: (a) and (b) Cross section of 0.2 vol-% CNC in polymer sample before and after field alignment. (c) In-plane alignment of CNC. (d) Single string of CB particles formed between two needle-shaped electrodes.

CONCLUSIONS

Electric or magnetic alignment of particles can be used to create nanostructured conducting composites. Such materials may find applications within the solar energy industry and in electrostatic discharge materials, battery, and sensor applications.

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