Rapid Communication

Fractal pattern formation in nanosuspension sessile droplets via evaporation-spreading on a glass substrate

M. Hadj-Achour *, D. Brutin *

Aix Marseille University, IUSTI UMR 7343, 13013 Marseille, France

A B S T R A C T

We report a fingering instability that occurs during the spreading and evaporation of a nanosuspension droplet. The patterns has a fractal structure similar to those reported by N. Shahidzadeh-Bonn and al. (2008) for salt crystallisation, during evaporation of saturated Na_2SO_4 on a hydrophilic surface. The fingering instability has been widely studied for both Newtonian and non-Newtonian fluids. However, this report describes the first time that a fingering instability is observed for the spreading of a nanosuspension sessile droplet. In this study, we demonstrate that in certain cases, the contact line evolves through different spreading regimes according to J. De Coninck et al. (2001) with an enhancement in the evaporation rate due the formation of the fractal patterns.

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Colloidal droplets exhibit different evaporation patterns that are similar to the so-called coffee-ring [3] or more complex networks of polygons, hexagonal arrays or uniform deposit.

A better comprehension of the behaviour of nanosuspensions is important to future developments of this technology. These materials are already involved in many applications, e.g., coating technologies, spray cooling and the manufacture of novel energy and electronic materials.

One of the most interesting subjects in nanotechnology is printed electronics, which has received a great deal of attention in recent years as a way of realising low cost electronic systems, such as displays, sensors and RFID tags. The fabrication quality is linked to the controllability of the printing process. To create a pattern using ink-jet printing technology, a chain of droplets with precisely controlled volumes must create lines with a constant diameter after evaporation. The resulting line should have a uniform and homogeneous constitution to avoid any undesirable resistivity.

In this letter, our experiments were performed using a commercial nano-suspension from the SunTronic Company. The physical proprieties given by the supplier for the different nanosuspensions are shown in Table 1.

* Corresponding authors. Tel.: +334 91 10 68 68; fax: +334 91 10 69 69.
E-mail addresses: miloud.hadj.achour@gmail.com (M. Hadj-Achour), david.brutin@univ-amu.fr (D. Brutin).

The experimental procedure consists of a few microlitres of the nanosuspension deposited gently on a glass substrate. The mass variation is recorded using a Mettler Toledo ×5105 Balance, which has a resolution of 10. The resulting patterns are recorded using a Canon 7D digital camera coupled with a 1 × 5 macro lens. The image analysis is performed using ImageJ software.

The evaporation is carried out in a Jacomex 314 litre G-Box-T2 Glove-Box, which is a covered parallel epipedic box measuring $100 \times 100 \times 150$ mm^3. It remained covered and has a humidity controller that remains off to avoid any external flow perturbations and to help reduce the noise level.

The volume of the droplets is approximately $2\,\mu L \pm 5\%$. The substrates were Thermo-Scientific microscope slides (Thermo Fisher Scientific, Inc.). To avoid particle aggregation, we used an ultrasonic tank. For each trial, we completely wetted the substrates. The average diameters of the droplets prior to the fractal pattern formation are approximately 11 mm ± 5%. We observe an instability leading to a fractal pattern as reported by N. Shahidzadeh-Bonn and al. for salt crystallisation [1], in nanosuspension #1 for larger diameters which can be observed in Fig. 1.

The experiments were conducted at the same conditions for all of the nanosuspensions listed in Table 1. For nano-suspensions #2 and #3, which have average nanoparticle sizes below 50 nm hydrodynamic wetting is the only phenomenon observed. This instability is observed for nanosuspension #1 when the average particle size is less than 150 nm.

Table 1
Physical proprieties of the SunTronic nanosuspensions.

#	Fluid nature	Average size	Concentration	Viscosity
Unite		nm	wt.%	$\frac{kg}{m \cdot s}$
1	Ethylene glycol	150	19	0.010
2	Triethylene glycol monomethyl ether	50	31	0.010–0.018
3	Tetradecane	10	52	0.008–0.014

Fig. 2 shows the dynamic droplet spreading of nanosuspension #1. The droplets from nanosuspensions #2 and #3 have patterns close to a circular form for all the evaporation experiments, while nanosuspension #1 displays a fractal pattern. (See Fig. 1.)

Brownian diffusion of nanoparticles [4,9] plays a major role in nanosuspension, where the competition between attractive and repulsive forces controls the equilibrium of the nanosuspension. When the nanosuspension droplet is deposited, the evaporation induces a decrease of the nanoparticles' free path leading to an aggregation of particles with a fractal growth.

The Diffusion Limited Aggregation (DLA) [15] is one of the most important models of fractal growth. The DLA model describes pattern formation by a series of simple rules. These rules are essentially a Brownian random walk of a single particle that wanders around an aggregate until it sticks to it after a collision. To improve the behaviour of the model, we added a sticking probability to modify the original DLA model, a compact fractal pattern is turned out. Hence, we assume that a part of the observed phenomena can be explained by the DLA model.

To compare with the experiments, a DLA simulation was performed. Fig. 2 shows the experimentally formed patterns.

Fig. 3 shows the evolution of $R^2(t) - R_0^2$ where R_0 is the initial radius. $R(t)$ is obtained from image analysis using ImageJ and based on the Feret diameter.

Fig. 3 shows the different stages of the evolution of the radius of the three nanosuspensions [8]. In the first stage, we observed a behaviour that is similar to power law evolution [10,7]. In the next stage, for nanosuspensions #2 and #3, we observed slow evolution of the square radius until they reached equilibrium. We identified three regimes for nanosuspension #1: an early, common regime of hydrodynamic-capillary wetting; a fast regime with a power law evolution, which we call the super-diffusion regime; and a final regime with a slow evolution, which we call the diffusive regime.

To quantify the evolution rate of the resulting patterns, where the key parameter can be defined as the perimeter evolution versus the surface area, we defined the geometric form factor and the perimeter gain [2]. The geometric form factor is based on the simple Euclidean relationship between the area and perimeter and can be expressed by the following equation:

$$D(t) = \frac{ln(A(t)/A_0)}{ln(P(t)/P_0)} \tag{1}$$

where P_0 and A_0 are, respectively, the initial perimeter and the initial surface, $P(t)$ and $A(t)$ are the measured perimeter and the measured surface, respectively. For a circle or a square, D = 2. When the geometric form factor is less than 1, the perimeter grows faster than its surface. Furthermore, $\dot{D}$ represents the evolution rate of the pattern.

The perimeter gain is defined as the ratio between the formed pattern perimeter and the equivalent circle perimeter calculated using the pattern area and can be expressed using the following relations:

$$G = \frac{P_{measured}}{P_{eq}} \tag{2}$$

$$P_{eq} = 2\sqrt{A_{measured}\pi}. \tag{3}$$

To characterise the evolution of the patterns, we calculated their geometric form factors at different times and the perimeter gain that results from the pattern; these results are shown in Fig. 4.

As shown in Fig. 4, for nanosuspensions #2 and #3, we found that D = 2; therefore, the patterns are circular during droplet evaporation. For nanosuspension #1, we observed a decrease in the geometric form factor. Consequently, the resulting pattern was a non-circular pattern with an equilibrium value of D = 0.76.

To examine the effects of the fractal patterns on the evaporation rate, we assume that droplet evaporation can be considered quasi-steady diffusion evaporation; therefore, the evaporation rate is given by the following equation:

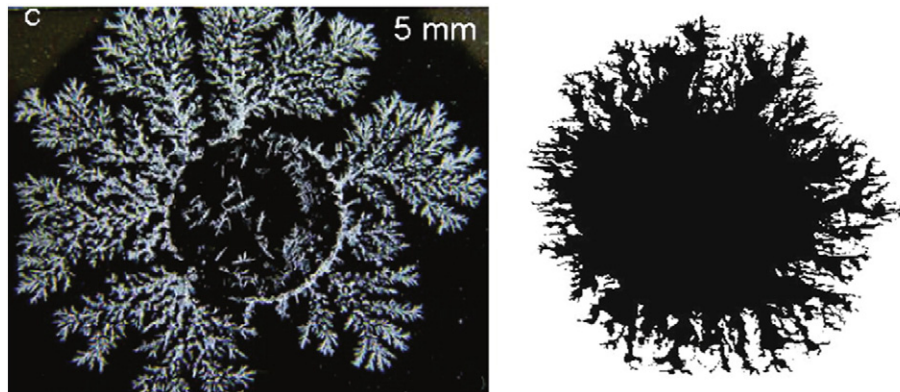$$\frac{dm}{dt} = 4\pi R D_{diff} \nabla C_v f(\theta) \tag{4}$$

Fig. 1. (Left) salt crystallisation pattern figure from [1]. (Right) the fractal pattern that results from the spreading of a sessile droplet of suspension #1.