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

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ABSTRACT

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.

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.

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 × 100 × 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 μL ± 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.

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Table 1
Physical proprieties of the SunTronic nanosuspensions.

#	Fluid nature	Average size	Concentration	Viscosity
Unite		nm	wt.%	$\frac{kg}{m\,s}$
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:

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

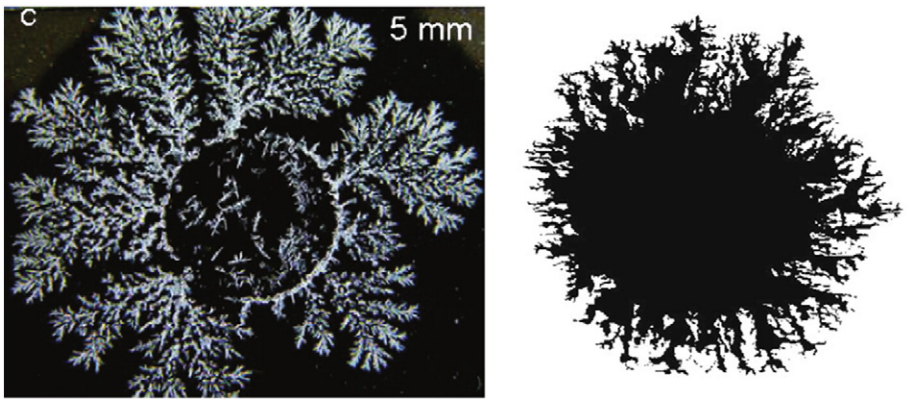

Fig. 1. (Left) salt crystallisation pattern figure from [1]. (Right) the fractal pattern that results from the spreading of a sessile droplet of suspension #1.

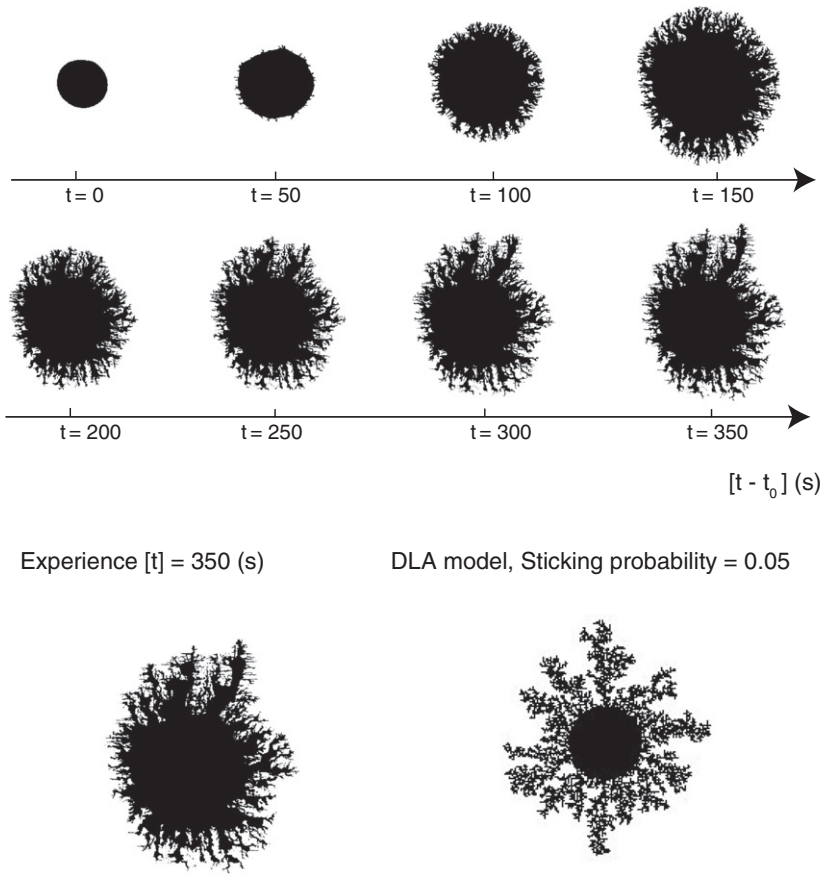

Fig. 2. Spreading evolution of a 2 droplet from nanosuspension #1. The DLA figure was obtained from a DLA model with a sticking probability of 0.05.

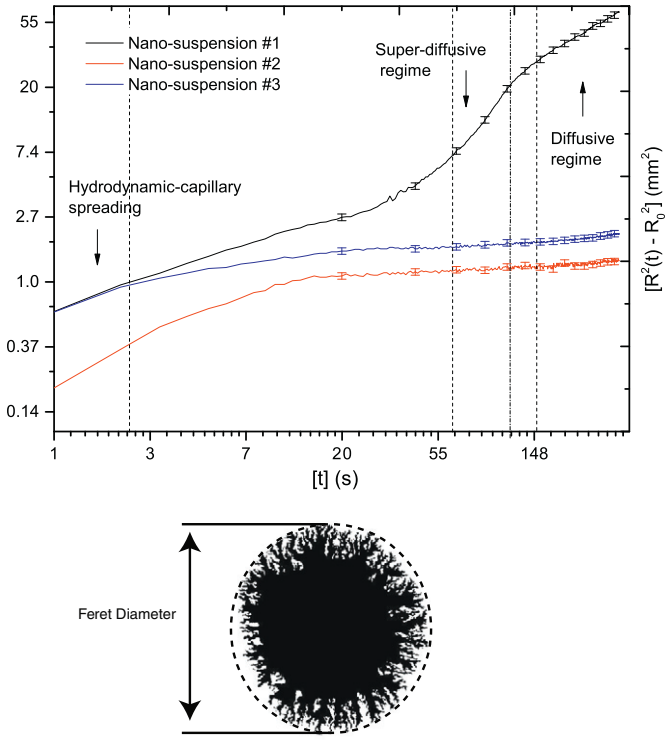

Fig. 3. Evolution of $R^2(t) - R_0^2$. The dashed lines separate the different spreading regimes. (The errors are provided for only a few points to ensure that the figure remains readable.).

where R is the radius, $f(\theta)$ is a function that depend on the contact angle (in the limit of small contact angles $f(\theta)$ can be approximated as 1.33), ∇C_v is the difference in the vapour concentration between the interfaces and is assumed to be saturated at the substrate temperature and zero far from the droplet. This model assumes that the droplet is isothermal with the substrate.

According to the quasi-steady diffusion evaporation model, the mass evolution shown in Fig. 4 clearly reveals the influence of the perimeter on the evaporation rate. For nanosuspensions #2 and #3, where the perimeter gain is approximately 1, the mass remains constant on the experimental time scale, while for nanosuspension #1, which has a positive perimeter gain, we clearly observe an increase in the evaporation rate due to the perimeter increase (G up to 8) as reported by N. Shahidzadeh-Bonn and al. [1] for salt crystallisation. The evaporation rate of nanosuspension #1 should increase during the experiment. We have to take into account the effect of the changing particle concentration in the quasi-steady evaporation model, which tends to slow the rate of evaporation [2,13], which explains the constant rate value.

This observation allows us to conclude that instability leads to an increase in the perimeter, which causes an increase in the evaporation rate. We also observed a clear relationship between the evolution of the geometric form factor and the evaporation rate. The total evaporation time and the equilibrium time of the geometric form factor, where $\dot{D} = 0$, agree well. This result allowed us to conclude that the observed phenomenon can be defined as an evaporation-spreading mechanism, where the effects of spreading and evaporation are coupled. Similar results have been observed for water-based nano fluids by Brutin [3], where the rates of evaporation influence the patterns formed during evaporation.

To investigate in detail the spreading regimes of nanosuspension #1, we fitted the experimental data in Fig. 3. The first regime, which we called "hydrodynamic-capillary wetting" has been widely studied [14,

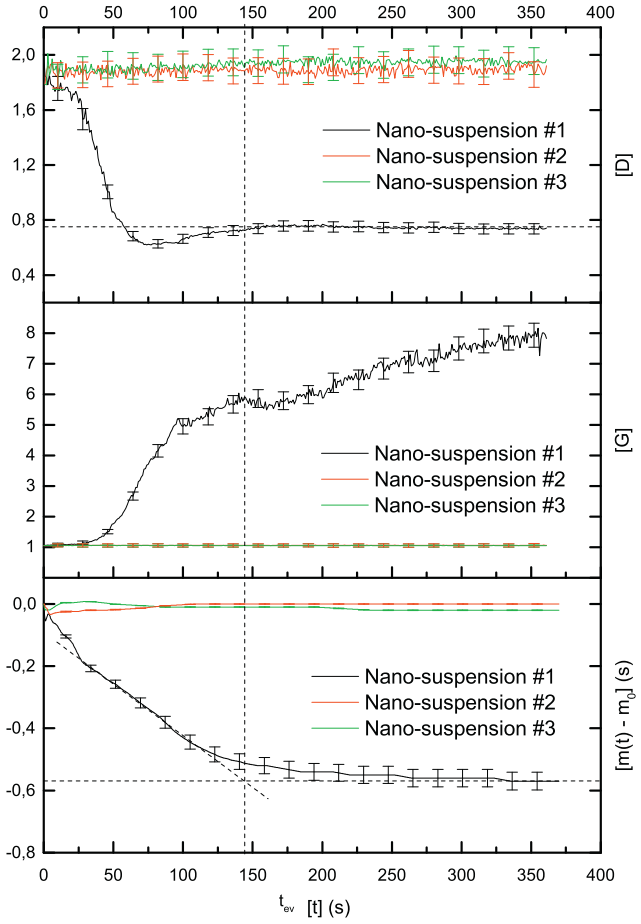

Fig. 4. Evolution of the geometric form factor, the perimeter gain and mass. (The errors are provided for only a few points to ensure that the figure remains readable.).

8,7], and the evolution of the contact line is given by Tanner's law. Therefore, we focused on the "super diffusive regime" and the "diffusive regime". Using a power law for the last regime, we obtained $\delta R^2 \propto t^{0.86}$. As reported by Pengtao et al. [12,11], this result can be explained by assuming that the spreading of the droplet is governed by a diffusion mechanism, where the mean squared displacement is described by a power law, $<\delta X^2(t)> \propto t^{\alpha}$. In a typical diffusion process, $\alpha = 1$. If $\alpha \neq 1$, then we have an anomalous diffusion. If $\alpha > 1$, the phenomenon is called super-diffusion, and if $\alpha < 1$, the particle undergoes sub-diffusion; the last regime is a sub-diffusion regime with $\alpha = 0.86$. Furthermore, this result allowed us to assume the existence of the super-diffusion regime [6], which can be the result of nanoparticle Brownian movement and an additional contribution due to evaporative flow.

For a free particle with a velocity $v = \dot{x}$ interacting with the surrounding fluid and exterior forces, by applying Newton's second law, we obtained the Langevin equation [5]:

$$mx = F_d + F_{th} + F_{hydro} \quad (5)$$

where m represents the particle mass, F_d is the friction force, F_{th} is the thermal noise and F_{hydro} represents the hydrodynamic force due to the evaporation flow.

According to the Langevin equation, for long time where $F_{hydro} = 0$, the squared position of a particle exhibits a linear evolution in time, for an initial position $x_0 = 0$, the square displacement is $\delta R^2 = 2Dt$. During the evaporation, $F_{hydro} \neq 0$, by fitting the Fig. 3 experimental data of the "super-diffusive regime", for the nano-suspension #1, we obtained $\delta R^2 \propto t^{1.806}$. This result justifies our assumption of the existence of a super-diffusion regime [6] with $\alpha = 1.806$, where evaporative flux enhances particle square displacement [3].

Finally, we confirm the evaporation-spreading nature of the fingering instability. Nevertheless, the role of the particle size, substrate and humidity still need to be studied. As reported by Brutin [3], for an iso-density water-based nano-fluid, the influences of the humidity, nanoparticle concentration and evaporation rate on the resulting pattern are important and lead to different pattern types. To understand the effects of the different physical proprieties, more experiments should be conducted.

To conclude, these experimental observations open new areas for investigation into the spreading behaviour of nanosuspension droplets on a substrate. The resulting patterns are similar to those for salt crystallization [1]. We found that the contact line exhibits different regimes with the presence of a super-diffusion regime. These results are a starting point for better understanding of the influence of nanoparticles on the evaporation of nanosuspension. We have great interest in improving the control of the spreading and evaporation of nanosuspensions.

References

[1] N. Shahidzadeh-Bonn, S. Rafaï, D. Bonn, G. Wegdam, Salt crystallization during evaporation: impact of interfacial properties, Langmuir 24 (2008) 8599–8605.
[2] M. Habibi, P. Moller, A. Fall, S. Rafaï, D. Bonn, Pattern formation by dewetting and evaporating sedimenting suspensions, Soft Matter 8 (2012) 4682–4686.
[3] D. Brutin, Influence of relative humidity and nano-particle concentration on pattern formation and evaporation rate of pinned drying drops of nanofluids, Colloids Surf. A 429 (2013) 112–120.
[4] A. Einstein, in: R. Fürth (Ed.), Investigation on the Theory of the Brownian Movement, Dover Publications, New York, 1926.
[5] P. Langevin, C.R. Acad. Sci. Paris 146 (1908) 530.
[6] B. Lukić, S. Jeney, C. Tischer, A.J. Kulik, L. Forr, E.-L. Florin, Direct observation of nondiffusive motion of a Brownian particle, Phys. Rev. Lett. 95 (2005) 160601.
[7] P.G. de Gennes, Wetting: statics and dynamics, Rev. Mod. Phys. 57 (1985) 827.
[8] M.J. de Ruijter, M. Charlot, M. Vou, J. Coninck, Experimental evidence of several time scales in drop spreading, Langmuir 16 (2000) 2363–2368.
[9] M. Rauscher, S. Dietrich, Wetting phenomena in nanofluidics, Annu. Rev. Mater. Res. 38 (2008) 143–172.
[10] J. De Coninck, M.J. De Ruijter, M. Vou, Dynamics of wetting, Colloid Interface Sci. 6 (2001) 49–53.
[11] D. Hang, D.M. Spelt Peter, Wetting condition in diffuse interface simulations of contact line motion, Phys. Rev. E 75 (2001) 046708.
[12] Y. Pengtao, Z. Chunfeng, J.F. James, Sharp-interface limit of the Cahn–Hilliard model for moving contact lines, J. Fluid Mech. 645 (2010) 279–294.
[13] Shengfeng Cheng, Gary S. Grest, Molecular dynamics simulations of evaporation-induced nanoparticle assembly, J. Chem. Phys. 138 (2013) 064701.
[14] L.H. Tanner, The spreading of silicone oil drops on horizontal surfaces, J. Phys. D Appl. Phys. 12 (1979) 1473.
[15] T.A. Witten Jr., L.M. Sander, Diffusion-limited aggregation, a kinetic critical phenomenon, Phys. Rev. Lett. 47 (1981) 1400–1403.