Multi-scale patterns formed by sodium sulphate in a drying droplet of gelatin: experiment and simulation in 2-dimensions

Tapati Dutta1,2, Sujata Taraafdar2 and Tajkera Khatun3,4
1 Physics Department, St. Xavier’s College, Kolkata 700016, India
2 Condensed Matter Physics Research Centre, Physics Department, Jadavpur University, Kolkata 700032, India
3 Physics Department, Charuchandra College, Kolkata 700029, India
E-mail: tajkera.khatun88@gmail.com

Abstract
We present a study of patterns, formed in drying drops of aqueous gelatin solution containing sodium sulphate. The patterns are highly complex, consisting of a hierarchical sequence of rings which form concentric bands as well as dendritic crystalline aggregates. We try to explain the origin of the rings and the dendritic growth from them, from a simple physical approach using the advection diffusion equations. We implement a finite difference scheme in 2-dimensions to simulate the experimental results. The effect on pattern formation using different solutions are examined by variation of contact angle and diffusivity. Our model can explain the growth dynamics of a complex pattern that covers several length scales, from the nano scale of single crystals, to the micro scale of dendrites and finally rings that are of the scale of centimeters.

1. Introduction
The crystallization patterns of salts in drying droplets shows a wide variety of intricate patterns [1–6]. Droplets of biological fluids when they are dried, also show different types of interesting patterns [7, 8]. Drying droplets of nano fluid shows transformation of nanorod into 3D fibre network [9]. Crystal formation on macroscopic scales to microscopic dendritic growth have been reported, ring formations like the well-known coffee stain and multiple rings have also been observed. The study finds applications in medical diagnostics, Annarelli et al [3], Sobac and Brutin [10], Shahidzadeh et al [5], ink-jet printing Paria et al [4] and drying of thin coatings. Flexible transparent conducting sheets have been fabricated using the coffee-ring effect Layani et al [11] and Shimoni et al [12], while interaction between droplets have been reported by Sanyal et al [13] and Cira et al [14]. Crack morphology is tailored in coffee-ring deposit via substrate heating by Lama et al [15], van Hameren et al [16] have reported the formation of self-organized hierarchical ring formation of porphyrin stacks on glass and mica substrates. They have proposed that the prominent rings are a result of the convective flow inside the droplet driven by evaporative flux. The finer rings between the main rings are deposited by a spinodal dewetting process following a dipole-dipole interaction between the constituent molecules. Shahidzadeh et al [5] have reported different crystal growth patterns for two salts and substrates. The authors propose that the emerging crystals determine whether the crystallization happens at the solid/liquid interface, the liquid/vapour interface or in the bulk. The size of the crystal clusters and their abundance determine whether the crystals form at the edge of the droplet as in CaSO4 or are swept inward as in NaCl.

One of the main constituents of Portland cement is sodium sulphate that crystallizes as thenardite (Na2SO4) or mirabilite (Na2SO4 · 10H2O), [17], depending on ambient conditions and water content. Rodriguez-Navarro et al [17] further show that crystallization pressure developed within porous materials when thenardite is formed, cause more damage to building material and rocks than formation of mirabilite. A metastable form, sodium hepta-hydrate (Na2SO4 · 7H2O), is also believed to be significant in this context, [17, 18]. So such studies are important from a practical point of view. If the salt solution in pure water is dried, a coffee-ring pattern [6] is observed. On highly hydrophilic surfaces, the salt forms dendritic patterns outside the drop initially deposited
This is due to a precursor wetting film surrounding the drop. The anhydrous salt crystallizes in rhombohedral form. If sodium chloride is dissolved in a complex viscous fluid e.g. containing a polymer, the dried drop shows more complicated features.

There are several models developed for complete understanding of drying droplet. Capillary flow in an evaporating sessile drop has been studied by Tarasevich by formulating an analytical model. Zigelman and Manor developed a model for pattern deposition of the solute from an evaporating droplet of dilute solution by taking into account the contact angle hysteresis and finite solubility. Evaporation of droplet is governed by film equation. This model explores the relationship between a variety of deposition pattern and the governing parameters.

When drops of aqueous gelatin solution containing sodium sulphate were allowed to dry on a glass substrate, Roy et al had reported an interesting observation: hierarchical series of concentric rings whose distribution is similar to a devil’s staircase, Mandelbrot. Once these hierarchical rings are deposited, dendritic crystal growths are observed between the rings. While the droplets of the size of ~1 cm in diameter, the ring thickness is of the ~μm and the dendrites are of the order of nm. To our knowledge we have not come across a single model that spans this multiscale range.

In this work we primarily try to understand the underlying physical processes that could be responsible for the complex pattern that droplets of aqueous Na₂SO₄ in gelatin display. We propose a 2-dimensional simulation model that reproduces the experimental observations. The motive here is to reproduce the general experimental pattern rather than an exact match with the pattern parameters. In this sense it is a general model that is expected to work with other combinations of solute and solvent, but are guided by similar physical processes. However our modelling is guided by the experimental findings of Roy et al.

Though the details of the experimental set-up and results are discussed in detail in Roy et al, in the next section we shall briefly describe their observations. The third section shall describe the 2-dimensional model in detail. This is followed by the section on results and discussions followed by conclusions.

### 2. Experiment and Observation

0.142 g of sodium sulphate powder was mixed with 50 ml de-ionized water, to get a solution of 0.02 M concentration. 0.5 g gelatin powder was mixed with this solution and stirred at temperature 60 °C until completely dissolved. A droplet of the solution of volume ~50 μl was deposited using a micro-pipette on a cleaned glass slide. The droplets were allowed to evaporate in a relative humidity (30–35)% and temperature 25 °C. Surface tension, viscosity and the angle of contact of the aqueous solution of Na₂SO₄ and gelatin were found to be 40.6 mN/m, 2.15 cP and 18 ± 2° respectively. The details of the experimental procedure are found in Roy et al.

Figure 1 shows the patterns of the drying droplets as observed under the microscope. The hierarchical ring pattern and the dendritic aggregates from the deposited rings is clearly visible.

### 3. Modelling and simulation

This section is divided into three subsections. The first subsection deals with the hierarchical ring formation, the second subsection is devoted to modelling the dendritic growth as we have observed that the dendrites grow...
from the rings after these have been deposited, [24]. We propose that the ring and dendritic structures occur in slightly different conditions, with the latter occurring when the droplet starts drying from around its edge. Our simulation however captures both the structure formations dynamically as the drying droplet evolves. We initially studied these patterns on a rectangular geometry with periodic boundary conditions to mimic the radial symmetry of the experimental set-up. et al. The third section illustrates the model on a circular geometry.

3.1. Simple model for hierarchical ring pattern
The internal mass flow in drying droplets can be very complex as many physical processes can occur simultaneously. The shape of the droplet is determined by the angle of contact at the triple line of contact. The ambient conditions that determine the diffusivity of vapour together with the angle of contact, is responsible for the evaporation flux at the droplet interface, which is highest at the triple line, [25, 26]. This results in a radially outward advective flow towards the edge, resulting in the well known ‘coffee ring effect’. At and near the ring of deposited salt, the concentration of salt in the solution is higher compared to the other regions of the droplet. Thus there arises a diffusive flux from the higher concentration to the lower salt concentration of the droplet. The juxtaposition of the advection and diffusion processes, causes the formation of a ring of salt in the region between the outermost ring and the centre of the droplet, when a critical concentration is reached. Critical concentration at any point is that concentration at and above which particles are deposited at that point. As the angle of contact remains the same, the droplet periphery now moves to the inner ring.

Advection is now limited to the droplet shape defined by the innermost ring, and as before, can form a new ring following the ‘coffee ring’ mechanism. In complex and highly viscous fluids like gelatin, the outer older rings do not dry out immediately. Kaya et al [19] had shown that the concentration of salt between consecutive rings was not symmetric. Therefore opposite diffusion fluxes in the region between consecutive rings may result in further deposition of rings. However these rings that may form, shall not be exactly midway between the two older rings, but placed closer to the hierarchically newer ring as the concentration there is higher. As long as there is a wet film of the solution between consecutive rings and the salt concentration sufficiently high to reach the critical value for precipitation, opposite diffusion fluxes will cause rings to deposit between older rings. This is responsible for the hierarchical ring structure observed in the experiment. Figure 2(a) shows a schematic representation of a deterministic model of the simple processes that have been described above.

3.2. Hierarchical ring pattern using stochastic modelling
A stochastic model of the dynamical processes responsible for the hierarchical rings is next discussed. We simulate the dynamics of droplet drying in a rectangular geometry, the length of the rectangle, along the j-direction, represents the initial radius of the droplet $R_i$, along any radial direction. The circular droplet geometry has axial symmetry which is mimicked in the simulation by applying periodic boundary conditions to the rectangular strip along its breadth, the i-direction. Therefore all variables in this rectangular geometry are functions of j-coordinate only, similar to the droplet geometry where the variables are symmetric about the cross-radial direction represented by $\phi$. We have adopted the evaporative flux expression of Deegan et al [27],
over the droplet interface. The velocity field distribution along the radius of the droplet is assumed to be proportional to the evaporative flux, and is given by

\[ v(r) \sim (R - r)^{-\lambda} \] (1)

and

\[ \lambda = (\pi - 2\theta)/(2\pi - 2\theta) \]

where \( \theta \) is the contact angle of the solution with the substrate, and \( r \) is the radius of any arbitrary point in the droplet. In the simulation any point \( r \) corresponds to a particular \( j \)-coordinate. Therefore we assume that the droplet dries with a fixed contact angle and the contact line is not pinned. The schematic of the drying droplet is shown in figure 3.

The solution is distributed uniformly on the square grid structure with a uniform concentration \( c_{in} \), and precipitation of the salt occurs only if a critical concentration \( c_{crit} \) is reached.

The advection equation in one dimension for variable velocity \( v \) and considering the concentration \( c \) as conserved scalar quantity is given by

\[ \frac{\partial c}{\partial t} + \frac{\partial (cv)}{\partial x} = 0 \] (2)

The advection equation for a variable velocity field is discretized and solved on the square grid using a finite difference scheme, and is given by

\[ c_{ij}^{t+1} = c_{ij}^t - (\Delta t/(2\Delta x))(v_{ij+1}^t c_{ij+1}^t - v_{ij-1}^t c_{ij-1}^t) \] (3)

Here \( i \) and \( j \) are the coordinates of the centre of each square grid whose size is defined by \( \Delta x \). \( \Delta x \) is taken small enough to ensure that the properties of concentration \( c_{ij} \) and velocity \( v_{ij} \) at the grid centre, are uniform throughout the grid. \( \Delta t \) is the value of unit time-step. The velocity boundary conditions are \( v_{0,0} = 0 \) at all times, and the singularity at the contact line is avoided by approximating \( v_{R,R} = 1.5v_{R-1,R} \) at all times. The concentration at every grid point is checked for critical value, which if reached, enables deposition at the site. The diffusion equation is discretized and solved at every grid point using the finite difference scheme and is given by

\[ c_{ij}^{t+1} = \alpha(c_{ij+1,j}^t + c_{ij-1,j}^t + c_{i,j+1}^t + c_{i,j-1}^t) + (1 - 4\alpha)v_{ij}^t \] (4)

where

\[ \alpha = D\Delta t/(\Delta x)^2 \]

Here \( D \) is the diffusivity of the solution. The system is again checked for critical concentration, which if reached, enables the salt to precipitate at the site. The innermost band that deposits, defines the outer boundary for the advection—diffusion process for the next time step. However diffusion is still allowed to continue between older deposited bands as long as it is not completely dry.

### 3.3. Dendritic growth between rings

The second part of the pattern simulation of the gelatin-\( \text{Na}_2\text{SO}_4 \) is concerned with the modelling of the dendritic growth observed at the deposited rings, figure 1(b). While the ring pattern is at macroscopic scales, of the order of centimeters, the dendrites are of micrometer dimensions. To model the dendrites which are evident after ring deposition, we start by assuming that there is no advection in the solution trapped between the rings that have already formed. However evaporation of the solution between rings occur leading to isolated droplets. These droplets no longer have a connected path to any of the precipitated rings. The concentration of dissolved salt in these droplets grows with increased evaporation and can precipitate \textit{in situ} if the concentration reach the critical value \( c_{crit} \). The isolated droplets are attracted towards the deposited salt rings with a force that is assumed to vary inversely as the cube of the distance between them. So a dipole dipole type attraction is assumed, without going into the microscopic origin of the attractive force. A particular isolated solution site \( G \), attaches itself to
where \( \Delta c \) is the concentration difference between the sites \( G \) and \( C \), \( r \) is the distance between them, \( S \) is the number of void sites counted up to the nearest and the second nearest neighbour sites with respect to the face of a crystal seed, and \( b \) is a parameter. The \( 1/S \) dependence of \( p_{\text{elec}} \) in the above equation represents the curvature of the growing crystal at the growth site. The parameter \( b \) lends the weight of the curvature to the dynamics. A higher positive \( b \) value will signify that more exposed growing tips of crystals are preferred as growth sites over others. The solute in these isolated droplets between rings, grow as dendrites. The mechanism of the growth process is described in detail in Dutta Choudhury et al.[2]. A brief outline of the algorithm is given for the sake of completeness.

1. A square lattice is placed within a circular boundary of radius 70 units. In the beginning, the gel sites \( G \) contain a certain concentration \( c \) of salt, besides gelatin and water, the concentration \( c \) at a site determined by the advection and diffusion processes discussed earlier. The crystal sites \( C \) are assigned a concentration of 1. The \( C \) sites make up the rings already deposited. Crystal growth is allowed only at nearest or second nearest neighbour sites of a \( C \) site.

2. Evaporation may occur at any \( G \) site with a probability \( p_e \). Upon evaporation, a \( G \) site is converted into a void site \( V \). The solute left behind at the site is distributed uniformly to all the connected \( G \) sites. In the case of an isolated \( G \) site, the solute gets deposited after evaporation of the solvent. However, the concentration of salt being insufficient for crystallization, it is deposited in amorphous form.

3. When the \( G \) site converts to \( C \), it is assumed that the salt in \( G \) contributes to the growing crystal, while the solvent content is distributed uniformly over neighbouring \( G \) sites.

4. The connectivity of the \( G \) sites is checked and all clusters of \( G \) sites are counted and labelled. To start with, there is one system spanning \( G \) cluster. As evaporation continues, isolated clusters of \( G \) sites surrounded by \( V \) sites appear. These are identified and labelled. The total number of \( G \) site clusters \( N_G(t) \) at any time step \( t \) is counted.

5. The clusters of \( V \) sites that are completely surrounded by \( G \) sites are identified and labelled and their number \( N_V(t) \) at any time step is also noted. In the beginning, this number is zero, but as evaporation proceeds, this number \( N_V(t) \) increases. After a while, \( N_V(t) \) starts decreasing as the void clusters start joining with each other and their number is thus reduced. When \( G \) sites no longer form a system-spanning cluster, the \( V \) sites must do so, since the system is 2-dimensional. With increasing time steps, the number \( N_V(t) \) increases while the number \( N_G(t) \) decreases.

6. At every time step we calculate the Euler number \( \chi(t) \), which is defined by

\[
\chi(t) = N_V(t) - N_G(t)
\]

The minimum of \( \chi(t) \) identifies the percolation threshold of voids. This signals the onset of the second mechanism for crystal growth, i.e., through attractive electrostatic forces.

7. Once the percolation threshold for voids is reached, growth through electrostatic forces is found to dominate over uniform crystal growth as in ring formation. The isolated \( G \) clusters are attracted towards the \( C \) cluster rings with a force that is assumed to vary inversely as the cube of the distance between them. So a dipole-dipole type attraction is assumed, without going into the microscopic origin of the attractive force. A particular \( G \) site attaches itself to one of the faces of the \( C \) site with a probability that is given by equation (5).

As long as the system is below the percolation threshold of the void clusters, a single time step skips the 7th step of the above procedures. Above the percolation threshold, all the steps enumerated above constitute a single time step. The net mass of the solute is conserved at every time step. In this simulation the parameter values were \( p_{\text{evap}} = 0.05, b = 7 \).

3.4. Modelling on circular geometry

The third section of our work involves the extension of the model to a circular geometry of the drying droplet. The 2-dimensional model now involves the \((r, \phi)\) coordinates. The finite difference scheme is implemented in solving the advection and diffusion equations with \( r \) varying from 0 to \( R \), with interval of 1 unit, \( R \) being the radius of the droplet. \( \phi \) is varied between \( 0^\circ - 360^\circ \), at intervals of unity. Periodic boundary condition is implemented along the cross-radial direction. The algorithm is identical to the \((i, j)\) system with
\[ i = r \cos \phi \]

and

\[ j = r \sin \phi \]

The grids now identified by \((r, \phi)\), increase in size with increasing \(r\) values, specially if \(R\) is large. The concentration, velocity and pressure values calculated at the grid centre, are assumed to be constant for the entire grid. This leads to a compromise in the precision of the values of these quantities in the outer grid points as compared to the internal points. However if \(R_i\) is kept small, one may approximate the precision to remain the same at all the grid points.

4. Results and discussions

The stochastic simulation has been carried out on a rectangular geometry of size \(3 \times 100\) units. Each square grid is of size \(\Delta x = 1.e^{-2}\) units, and \(\Delta t = 0.25 \times 1.e^{-4}\) units represents time unit in the advection and diffusion processes, keeping the von Neumann stability criteria intact [28]. The angle of contact \(\theta = 65^\circ\), and kept constant and diffusion coefficient of the solution \(D = 1.5\) unit, to obtain a pattern that best matches the experimental results. In our simulation, the angle of contact \(\theta\) determines the droplet shape for fixed ambient conditions, which in turn determines the evaporative flux and therefore the velocity field. Thus \(\theta\) and \(D\) control the fluid transfer in the droplet and are parameters of the model. The initial salt concentration \(c_{in} = 0.78\) and the critical concentration \(c_{crit} = 0.8\), are the other parameters of the model. For the 2-dimensional circular model, \(R_i = 50\) units.

The effect of variation of the angle of contact for fixed value of \(D = 1.5\) unit, is shown in figure 4. The initial coffee-ring like deposit is formed in each case, however the spacing between the rings is evidently strongly dependent on angle of contact. The patterns obtained for \(\theta = 65^\circ\) show the hierarchical pattern observed in experiment of gelatin and sodium sulphate dry droplet, figure 1. The effect of the variation of the diffusion coefficient of the solution on pattern formation is depicted in figure 5 keeping the angle of contact fixed at \(\theta = 65^\circ\), as this angle of contact was found most suitable from the previous study. It appears that the hierarchical rings obtained in the experiments of Roy et al [22], are better reproduced by \(D = 1.5\) units, figure 5(e). In figures 6(a) and (b), the ring spacing for different values of the contact angle and diffusion coefficient of

---

**Figure 4.** Effect of variation of angle of contact for fixed \(D = 1.5\) unit. Figures (a) to (d) represent respectively \(\theta\) values of 0.3, 3.0, 65 and 80 degrees. The blue colour denotes the solution, the red and blue colours of the rings denote deposition after advection and diffusion processes respectively. Colours visible online.
solutions, are shown respectively. The figures indicate that the step lengths change for different solution characteristics. The step like clustering of the ring pattern is testimony to the hierarchical ordering of the deposited rings. This also matches the experimental results reported by Roy et al [22].

Figure 7 shows the concentric ring patterns that develop in a circular 2-dimensional system of the model for different values of $D$. The angle of contact is maintained at the constant value $\theta = 65^\circ$ as before. In this case the hierarchical ring pattern is better reproduced for lower $D$ values, $\sim 10^{-3}$. At higher values of $D$, the hierarchical pattern is destroyed.

The formation of dendrites is observed once the crystal rings have deposited. In the simulation, the parameter $b = 12$ in equation (5). The time development of dendrite formation along deposited rings from the simulation study is shown in figure 8. The figure represents an enlarged picture of the dynamics between consecutive rings. While some of the isolated droplets deposit their solute content as the growing dendrites, shown in green colour online, others may deposit the solute in situ, shown in black online, if the critical concentration $c_{crit}$ is reached due to the evaporation of the droplet. These deposits may be single crystals of nanometer scale, Dutta Choudhury et al [2]

From the series of pictures in figure 8, it is clear that the dendrites grow at the cost of evaporating solution from between rings. Experimental observation of the dendritic growth of salt aggregates from deposited rings is shown in figure 1(b).
5. Conclusions

We have demonstrated the formation of a multiple band pattern, that mimics the multiple rings formed on a drying droplet of aqueous gelatin with sodium sulphate. The model was developed initially on a rectangular geometry and later extended to a circular geometry. As the drying droplet has axial symmetry, in the first case, the rectangular bands represent the dynamics along any radial section of the droplet. The bands form a hierarchical sequence of rings which are reminiscent of the ‘Devil’s Staircase’ pattern. The hierarchical ring pattern of the salt is reproduced taking into account advection in conjunction with diffusion. With continued evaporation of the solution between deposited rings, isolated droplets of solution which are $\sim\mu$ scale, separate. We propose an electrostatic attraction between these tiny droplets and the salt crystals on the rings. These are attracted to a crystal seed on the ring where they attach with a probability that is dependent on the concentration gradient between the sites, the curvature of the site at the point of attachment and inversely proportional to the distance between the sites. This results in highly branched dendritic aggregates that growing from the rings. The whole pattern therefore encompasses multiple scales from nano-sized single crystals to micron-sized dendrites and finally rings with diameter of the order of centimeters. This complicated dynamics has been modelled by using convection and diffusion processes in conjunction. We have neglected strong temperature gradients and substrate effects. The model is a qualitative attempt to reproduce the complex pattern observed at different scales when $\text{Na}_2\text{SO}_4$ solution in gelatin is allowed to dry as droplets. The motivation was to understand the main physical processes that are responsible for this kind of pattern. The surface tension and viscosity do not explicitly enter in the equations used in this model. However it may be argued that a greater value of surface tension will
result in a higher value of contact angle for the same substrate. Equation (1) of Deegan et al proposes this velocity distribution which is controlled by the evaporation flux at the droplet surface. The presence of the gel increases the viscosity of the solution and reduces the convective flux to the edge. This will affect the rate at which the rings form, perhaps the pattern itself. There are further plans to develop the model in 3-dimensions incorporating these features.

Acknowledgments

The authors are grateful to Mr Biswajit Roy, Assistant Professor at Chakdaha College, for experimental inputs.

ORCID iDs

Tapati Dutta @ https://orcid.org/0000-0002-8641-9712

Tajkera Khatun @ https://orcid.org/0000-0003-0059-5430

References

[1] Dutta Choudhury M, Dutta T and Tarafdar S 2013 Pattern formation in droplets of starch gels containing NaCl dried on different surfaces Colloids Surf. A 432 110
[2] Dutta Chowdhury M, Dutta T and Tarafdar S 2015 Growth kinetics of NaCl crystals in a drying drop of gelatin: transition from faceted to dendritic growth Soft Matter 11 6938
[3] Annarelli C C, Fornaziero J, Bert J and Colombani J 2001 Crack patterns in drying protein solution drops Eur. Phys. J. E 55 599
[4] Parija S, Ghosh Chaudhuri R and Jason N N 2014 Self-assembly of colloidal sulfur particles on a glass surface from evaporating sessile drops: influence of different salts New J. Chem. 38 5943
[5] Shahidzadeh N, Schut M F L, Desarnaud J, Prat M and Bonn D 2015 Salt stains from evaporating droplets Sci. Rep. 5 10335
[6] Shahidzadeh-Bonn N, Rafii S, Bonn D and Wegdam G 2008 Salt crystallization during evaporation: impact of interfacial properties Langmuir 24 8599
[7] Tarasēvič Y Y and Pvatolavnovna D M 2007 Segregation in desiccated sessile drops of biological fluids Eur. Phys. J. E 22 311–4
[8] Brütin B, Sobac B, Loquet B and Sampol J 2011 Pattern formation in drying drops of blood J. Fluid Mech. 667 85–95
[9] Wu H, Chen L, Zeng X Q, Ren T H and Briscoe W H 2014 Self-assembly in an evaporating nanofluid droplet: rapid transformation of nanorods into 3D fibre network structures Soft Matter 10 5243
[10] Sobac B and Brütin D 2011 Structural and evaporative evolutions in desiccating sessile drops of blood Phys. Rev. E 84 011603
[11] Layani M, Gruchko M, Milo O, Balberg I, Azuday D and Magdassi S 2009 Transparent conductive coatings by printing coffee ring arrays obtained at room temperature ACS Nano 3 3537
[12] Shimoni A, Azoubel S and Magdassi S 2014 Inkjet printing of flexible high-performance carbon nanotube transparent conductive films by coffee ring effect Nanoscale 6 11084
[13] Sanyal A, Rau S, Chowdhuri S, Kabi P and Chaudhuri S 2014 Precision control of drying using rhythmic dancing of sessile nanoparticle laden droplets Appl. Phys. Lett. 104 163108
[14] Cira N J, Benuisiglio A and Prakash M 2015 Vapour-mediated sensing and motility in two-component droplets Nature 519 446
[15] Lama H, Basavaraj M G and Satapathy D K 2017 Tailoring of crack morphology in coffee-ring deposits via substrate heating Soft Matter 13 5445–52
[16] van Hameren R, Schon P, van Buul A M et al 2006 Macroscopic hierarchical surface patterning of porphyrin trimers via self-assembly and dewetting Science 314 1433
[17] Rodrigues-Navarro G, Doehne E and Sebastian E 2000 How does sodium sulfate crystallize? Implications for the decay and testing of building materials Cement and Concrete Research 30 1527
[18] Hamilton A, Hall C and Pei L 2008 Sodium sulfate heptahydrate: direct observation of crystallization in a porous material J. Phys. D: Appl. Phys. 41 212002
[19] Kaya D, Beliy V A and Muthukumar M 2010 Pattern formation in drying droplets of polyelectrolyte and salt J. Chem. Phys. 133 114905
[20] Tarasēvič Y Y 2005 Simple analytical model of capillary flow in an evaporating sessile drop Phys. Rev. E 71 027301
[21] Ziegelman A and Manor O 2016 A model for pattern deposition from an evaporating solution subject to contact angle hysteresis and finite solubility Soft Matter 12 5695
[22] Roy B, Dutta Choudhury M, Dutta T and Tarafdar S 2015 Multi-scale patterns formed by sodium sulphate in a drying drop of gelatin Appl. Surf. Sci. 357 1000
[23] Mandelbrot B B 1977 Fractal Geometry of Nature (New York: W H Freeman & Co.)
[24] sodium sulfate in gelatin https://youtu.be/kyUSWdDnUXU
[25] Hu H and Larson R G 2002 Evaporation of a sessile droplet on a substrate J. Phys. Chem. B 106 1334
[26] Popov Y O 2005 Evaporative deposition patterns: spatial dimensions of the deposit Phys. Rev. E 71 036313
[27] Deegan R D, Bakajin O, Dupont T F, Huber G, Nagel S R and Witten T A 1997 Capillary flow as the cause of ring stains from dried liquid drops Nature 389 827
[28] Charney J G, Fjortoft R and von Neumann J 1950 Numerical integration of the barotropic vorticity equation Tellus: A quarterly Journal of Geophysics 2 237