Equidistant band formation of precipitation in a reaction–diffusion process

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Abstract. We study precipitation patterns occurring in diffusion-limited reactions, focusing on Liesegang bands. Naturally, these patterns are non-equidistantly spaced, and thus less useful for bottom-up material design. However, we show how a continuous large-scale modification of the inhomogeneity of the substrate and/or the nucleation threshold can be used to obtain equidistantly spaced bands on small length scales. We confirm our suggestions by lattice-gas simulations and propose an iterative experimental procedure not requiring a priori knowledge of parameters. We discuss the feasibility for glass substrates modified by irradiation with femtosecond laser pulses.

Natural pattern formation can be found in many systems on various length scales [1] and with many shapes and types [2]. Besides the aesthetic appeal of the patterns, efforts are driven by the idea of designing devices in a bottom-up approach [3]–[6]. One aims at understanding and controlling the pattern formation processes to design materials with patterns for special applications. Although such an approach is complementary to top-down approaches such as lithography, a combination of both seems to be most promising for applications. For example, lithography can be used to design structures in the two lateral dimensions on the surface of a sample. However, in order to design structures and material properties in the third dimension of the sample, i.e. in the direction perpendicular to the surface, a different approach is needed.

One of the promising phenomena for creating well-defined structures in a bottom-up approach is Liesegang pattern formation [3], [7]–[17]. Liesegang rings or bands typically form if a substance diffuses from a centre or a peripheral edge into an initially homogeneous medium,
where the reaction product precipitates and aggregates. The phenomenon is observed on macro-
scopic length scales (centimetres), typically for reaction–diffusion systems in gels [16, 17], but
also in micrometre [3, 12, 14, 15] and nanometre regimes in solid materials [13].

In this paper, we study modified Liesegang pattern formation theoretically and by means of
computer simulations. We show that a continuous large-scale modification of the inhomogeneity
of the substrate before the actual reaction–diffusion process can be used to control the positions
of the Liesegang bands in the direction perpendicular to the surface of the sample. In addition,
we discuss the experimental feasibility of our suggested approach for Liesegang patterns of
metal nanoparticles in glassy materials, which have been observed experimentally [13]. In
such samples, the substrate can be modified by irradiation with femtosecond laser pulses (see
e.g. [18]–[21] and references therein). These modifications can affect the refractive index,
the absorption coefficient, the nonlinear optical susceptibility, the crystal structure [22, 23]
and, last but not least, the precipitation processes of nanoparticles [24]–[27]. However, the
spatial resolution of such a modification technique may remain rather broad (micrometre
resolution) and therefore fast if it is merely used to set the stage for the actual bottom-up
structuring process based on Liesegang pattern formation. Afterwards, lithographic or even
electrical [28, 29] techniques can be used to generate structures in the two lateral dimensions
of the sample. Additionally, the properties of the nanoparticles forming the Liesegang bands
could be modified [30, 31].

Liesegang patterns are quantitatively described by three laws governing the creation time
t_\alpha, the distance x_n from the surface of the sample and the width w_n of the nth band: time law
x_n \propto \sqrt{t_\alpha}, spacing law x_{n+1} = (1 + p)x_n and width law w_n \propto x_n^\alpha (see [32] for a recent review). These
laws have been derived in mean-field approaches based on (i) reaction–diffusion models with a
threshold [33]–[35] and (ii) phase-separating models with spinodal decomposition [36, 37].

Here we show that it is possible to obtain equidistantly spaced patterns by changing the
coefficient p of the spacing law in a controlled fashion in space or in time. We derive a general
approach, which is independent of a specific detailed reaction process and does not need a priori
knowledge of any process parameters. We achieve equidistant patterns by preparing a substrate
either with a gradient in the density of nucleation seeds or with a gradient in the strength of
heterogeneities. Our approach is based on a theoretical formula for the spacing-law coefficient
p originally derived in a mean-field model [34] and recently extended to include several different
types of fluctuations [38]. We verify our predictions in a microscopic lattice–gas simulation [32],
[38]–[40] and discuss their experimental feasibility.

We define a pattern to be equidistantly spaced if the distance between the centres of
all neighbouring bands is identical, i.e. x_{n+1} = x_n + \Delta_x for all n; see figure 1 for illustration.
Inserting the spacing law x_{n+1} = (1 + p)x_n yields the spatial dependence of the coefficient p,

\[
p(x) = \Delta_x / x.
\]

Since the Liesegang bands are created successively in space and time according to the time law,
it is possible to transform equation (1) into a temporal version, i.e. p(t), if the reaction profile
is known.

Although equation (1) ensures that the spatial distances between the bands are identical,
their widths w_n will not be the same. The reason is that w_n depends not only on p but also on the
density d_n of precipitated particles in the nth band. Because of particle conservation, we have
w_n \propto p x_n / d_n [32, 37]. Naturally, one finds w_n \propto x_n^\alpha with \alpha \leq 1 [32, 33, 39, 40]. Therefore, the
density usually increases with the position of the band as d_n \propto x_n^{1-\alpha}. For equidistant bands, on
Figure 1. Two-dimensional representation of the three-dimensional Liesegang patterns with equidistant spacing obtained in lattice–gas simulations on a cubic lattice (32 × 32 × 2048). All 32 slices (in the z-direction) are plotted next to each other vertically (in the y-direction). Grey dots represent mobile C and white dots represent precipitated D particles; A (not shown) diffused into the volume from the left. Equation (1) is fulfilled (a) by spatial variation of the nucleation threshold $K_{sp}(x)$ or (b) by spatial variation of the strength of heterogeneities. The simulation parameters are as follows: (a) $c_0 = 107.2$, $D_f = 1.22$, $D_C = 0.1$, $K_p = 19$, $F_1/\Delta x = 0.01$ and $F_2 = 1$ for equation (3), and (b) $c_0 = 107.2$, $D_f = 1.22$, $D_C = 0.1$, $K_{sp}^{\text{het}} = 111$, $K_p = 37$, $F_1/\Delta x = 0.005$, $F_2 = 1.1$ and $F_2'' = 2.8$ for equation (4).

The other hand, this implies a decrease of the bandwidths, since $w_n \propto \Delta x/d_n \propto s_n^{\beta - 1}$. This is confirmed in the simulations shown in figure 1. However, the mass $m_n = w_n d_n$ of the bands is expected to be constant for equidistant bands. Nevertheless, the time law remains unchanged unless the diffusion process is modified in space or time.

Using equation (1), it is possible to obtain equidistant banding if the $p$ dependence of one or more parameters of the reaction–diffusion process is known and if these parameters can be changed systematically in space and/or in time. It is even sufficient to know the dependences in an empirical way. Parameters that could be varied include temperature, boundary conditions, concentrations of reacting particles, etc. An alternative approach, however, is the spatial variation of the substrate to impose the required $p(x)$. For example, a change of the dimensionality, i.e. a fractal structure, would alter the diffusivity in space and time (fractal diffusion law).

Another possibility—the one we study here—is the spatial modification of the inhomogeneities or defects in the substrate, since nucleation and precipitation are altered by them. Experimentally this could be achieved e.g. in glass substrates by irradiation with intense laser pulses in order to control Liesegang pattern formation of metal nanoparticles [13]. Since a broad (large-scale) gradient of inhomogeneities induced in the substrate before the actual reaction–diffusion process will be sufficient for equidistant banding on the micrometre scale (or below), this procedure can be regarded as real bottom-up pattern formation. It is complementary to approaches directly interfering with the detailed chemical reaction–diffusion processes in a homogeneous substrate [41].

We base our approach for equidistant patterns on a theoretical formula for the spacing-law coefficient $p$ originally derived in a mean-field model [34] and later extended by three empirical approximations to include the effects of a growth threshold for the precipitates, thermal fluctuations of the particle densities and random spatial fluctuations of the nucleation
The underlying nucleation and growth model for Liesegang pattern formation (see [32] for a review) assumes that one substance (B) is initially homogeneously distributed in the substrate and reacts with the other substance (A) diffusing into the sample from one surface. The reaction product (C) is mobile, but precipitates to form immobile particles (D) if its local concentration exceeds the nucleation threshold $K_{sp}$. In addition, the D particles grow at the expense of C as long as the local concentration of C remains above the growth threshold $K_p$. In this scenario, the spacing-law coefficient is given by [38]

$$ p = F_1 \frac{D_C}{D_t} \left( \frac{F_2 c_0}{K_{sp}} - 1 - \frac{D_C}{2D_t} \right)^{-1}, \quad (2) $$

with $D_t$ the effective diffusion coefficient of the reaction zone, $c_0$ the limit concentration of C (both of which can be calculated self-consistently from the initial concentrations and diffusivities of A and B) and $D_C$ the diffusivity of C. $F_1$ and $F_2 = 1 + F_i^2/\sqrt{c_0}$ are empirical parameters approximating influences of the bandwidths (controlled by $K_p$) and thermal fluctuations, respectively.

Inserting equation (1) into equation (2), it is easy to find the required spatial gradient of the nucleation threshold,

$$ K_{sp}(x) = F_2 \frac{c_0}{D_C} \left( \frac{F_1}{\Delta x} + \frac{D_t}{D_C} + \frac{1}{2} \right)^{-1}. \quad (3) $$

Figure 2 depicts $K_{sp}(x)$ for the parameters of the simulation shown in figure 1(a). Clearly, $K_{sp}(x)$ is decreasing with depth x from the substrate surface. However, the necessary decay is, in general, not a simple exponential as has been recently suggested for a specific detailed reaction process [42]. In order to optimize the number of Liesegang bands, the parameters, in particular $D_t/D_C$, must be tuned such that $K_{sp}(x)$ decreases slowly.

Since the nucleation threshold might be difficult to modify directly in experiments, we also study—as a second alternative—inhomogeneous nucleation with $K_{sp}$ randomly fluctuating in space. In this case, it is sufficient to impose a gradient onto the width of the random fluctuations of $K_{sp}$, which corresponds to imposing a gradient on the inhomogeneity of the substrate. We consider a Gaussian distribution of $K_{sp}$ values with average $K_{sp}^{\text{het}}$ and standard deviation $\sigma$ [38]. Then an effective threshold $K_{sp}^{\text{eff}}$ can be approximated by $K_{sp}^{\text{het}} - F_2^{sp} \sigma$ with an empirical parameter $F_2^{sp}$. Inserting $K_{sp}^{\text{eff}}$ into equation (2) and using again equation (1), one obtains

$$ \sigma(x) = \frac{K_{sp}^{\text{het}}}{F_2^{sp}} - F_2^{sp} \frac{D_C}{D_t} \left( \frac{F_1}{\Delta x} + \frac{D_t}{D_C} + \frac{1}{2} \right)^{-1}. \quad (4) $$

To achieve equidistant banding in this way, the constraint $0 < \sigma(x) \ll K_{sp}^{\text{het}}$ must hold, since the fluctuations cause random nucleation without banding if $\sigma$ is in the order of the mean nucleation threshold $K_{sp}^{\text{het}}$. However, $\sigma(x)$ will eventually reach the mean nucleation threshold for large $x$ according to equation (4). Therefore, the parameters determining the gradient of $\sigma(x)$ must be chosen such that $\sigma(x) \ll K_{sp}^{\text{het}}$ within the length of the sample. Figure 2 shows the $\sigma(x)$ used in the simulation depicted in figure 1(b). Because the pattern formation does not start at $x = 0$ one does not need $\sigma(x) > 0$, for small $x$.

Next we test our suggestions for equidistant Liesegang bands in a microscopic simulation. We impose equation (3) or (4), i.e. the gradients of $K_{sp}(x)$ or $\sigma(x)$ shown in figure 2, into a lattice-gas simulation of the nucleation and growth model described above. We refer to [32, 38].
Figure 2. Spatial dependence of $K_{sp}(x)$, solid line, and $\sigma(x)$, dashed line, used for obtaining equidistantly spaced Liesegang bands (same parameters as in figure 1).

Figure 3. Characterization of the bands depicted in figure 1, red symbols for homogeneous nucleation and yellow symbols for heterogeneous nucleation. (a) Individual inter-band distances $\Delta x_{n,n}$ (triangles) and masses $m_n$ (circles). The corresponding means and standard deviations are $\Delta x = 30.1 \pm 0.8$ and $51.8 \pm 3.0$ lattice points and $m = 2919 \pm 107$ and $4957 \pm 421$ particles for homogeneous and heterogeneous nucleation, respectively. (b) Bandwidths $w_n$ (circles) and densities $d_n$ (squares).

for a detailed description of the simulation procedure; note that $K_{sp}$ and $\sigma$ are kept constant in these previous papers. Figure 1(a) shows a representative result for homogeneous nucleation (spatial gradient $K_{sp}(x)$, $\sigma = 0$), while figure 1(b) is obtained with heterogeneous nucleation (constant $K_{sp}^{\text{het}}$, spatial gradient $\sigma(x)$).

Figure 3(a) confirms that the individual inter-band distances $\Delta x_{n,n} = x_{n+1} - x_n$ and the masses $m_n = w_n d_n \approx c_0 \Delta x_{n,n}$ are approximately constant. Figure 3(b) confirms that the widths $w_n$ decrease with depth, while the densities $d_n$ increase. The equidistant bands formed by homogeneous or heterogeneous nucleation are fully equivalent, the numerical differences in $\Delta x$ and $m_n$ being merely due to the chosen parameters. However, it is harder to achieve a low variance of $\Delta x_{n,n}$ and $m_n$ in the case of heterogeneous nucleation (see the caption of figure 3).

The presented results of unbiased equidistant patterns have not been achieved in an ad hoc manner. We have rather obtained them following an optimization scheme, which is described next. Such a scheme is necessary since the empirical parameters $F_1$, $F_2$ and $F_2''$ are not only unknown, but they also depend on $K_{sp}$ [38]. To make things worse, the positions $x_n$ of the bands
are affected by an offset $\xi$ in both experimental and simulation results, such that the theoretical positions $x_n$ are related to the measured $x'_n$ by $x_n = x'_n + \xi$ [32]. Equation (1) thus has to be rewritten as $p(x') = \Delta_x/(x' + \xi)$ with a $\xi$ that is not known beforehand. The latter change also affects equations (3) and (4), where $x$ must be replaced by $x' + \xi$.

Nevertheless, it is possible to achieve equidistant banding in an iterative procedure not requiring a priori knowledge of the parameters $\xi$, $F_1$, $F_2$ and $F_2''$ (for heterogeneous nucleation only). Therefore, we are convinced that this procedure will also be applicable in experiments where the nucleation and growth model is not describing the processes exactly. Such a practical approach is consistent with bottom-up material design, since a full quantitative understanding of the process is not needed, if the desired structures can be obtained reliably.

We start the iterative procedure with arbitrary $F_1/\Delta_x$, $F_2$, $F_2''$ and $\xi' = \xi + \delta \xi$, replacing $x$ by $x' + \delta \xi'$ in equations (1), (3) and (4). Since the error in guessing $\xi$ is most crucial, we denote it as $\delta \xi$ here. The errors caused by incorrect $F_1/\Delta_x$, $F_2$ and $F_2''$ can also be dealt with approximately via $\delta \xi$, as will be shown below. The bias error $\delta \xi$ causes a wrong spacing of the bands $x'_{n+1} - x'_n = x_{n+1} - x_n = p x_n = \Delta_x (x'_n + \xi')/(x'_n + \xi')$, i.e.

$$
(x'_{n+1} - x'_n)(x'_n + \xi') = \Delta_x (x'_n + \xi') - \Delta_x \delta \xi.
$$

(5)

If the measured band positions $x'_n$ of an experiment yield a linear plot according to this equation, both $\Delta_x$ and $\delta \xi$ can be extracted from the linear fit; see figure 4(a). Then it is possible to reduce the linear trend in the inter-band spacings (due to $\delta \xi \neq 0$) by variation of $\xi'$ in the next iteration of the experiment. On the other hand, if the plot according to figure 4(a) and equation (5) is not approximately linear, the information on the reaction process is insufficient to achieve equidistant banding.

Figure 4(b) shows that the bias error $\delta \xi$ can be eliminated by optimizing $\xi'$. Basically, one has to determine a few points in the plot and find the zero of $\delta \xi(\xi')$, which corresponds to finding the real $\xi$. Note that the final value of the inter-band spacing $\Delta_x$ is not known initially. Hence, several runs with different $F_1/\Delta_x$, $F_2$ and possibly $F_2''$ might be needed until a requested value of $\Delta_x$ can be obtained. This is shown in figure 4(c), where the $\Delta_x$ obtained for optimized equidistant spacing (optimized $\xi' = \xi$) is plotted for several values of $F_1/\Delta_x$ and three values of $F_2$ (homogeneous nucleation) as well as for two sets of values of $F_2$ and $F_2''$ (heterogeneous nucleation). The figure confirms that our optimization procedure can be applied for very different parameter sets. It suggests that the procedure might also work for Liesegang pattern formation in systems where the nucleation and growth model is not the best modelling approach. In the experimental procedure, appropriate values for the parameters can be found iteratively, using plots like those in figure 4. Although this procedure could be quite cumbersome and a bit time consuming (depending on the actual materials and processes), the method should work once parameters have been adjusted. This would justify the experimental effort.

Of course, an experimental verification of our suggested procedure would be highly welcome. We sincerely hope that this paper can stimulate work in such a direction. Regarding experimental feasibility, we discuss the special case of metal nanoparticles in glassy materials modified by irradiation with femtosecond laser pulses here. On the one hand, normal Liesegang pattern formation with non-homogeneously spaced bands has been observed experimentally and pictured by electron microscopy in such samples [13]. Repeating these experiments under modified conditions (temperatures, concentrations, etc) yielded samples with different distances of Liesegang bands as well as different numbers of bands [43], illustrating the possibility of modifying the patterns.

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Figure 4. (a, b) Analysis and optimization of the bias parameter $\delta \xi$ for obtaining equidistant bands, red symbols for homogeneous nucleation and yellow symbols for heterogeneous nucleation. (a) Fits of equation (5) (black lines) to the data of $x_n$ (circles) with $\xi' = -44$ and $-103$ for homogeneous and heterogeneous nucleation, respectively. The fits yield $\Delta_x = 30.0$ and $50.4$ with bias parameters $\delta \xi = -0.75$ and $-26.85$, respectively. (b) Bias parameters $\delta \xi$ versus $\xi'$ as extracted from plots similar to the one shown in (a) and averaged over three configurations. (c) Optimized $\Delta_x$ for homogeneous nucleation (small symbols) and heterogeneous nucleation (large symbols). The parameters $c_0 = 107.2$ and $D_I = 1.22$ are identical for all results. We used $D_C = 0.1$, $K_p = 19$, and $F_2 = 0.8$ (red circles), $1$ (light green diamonds) and $1.25$ (dark green squares) for homogeneous nucleation and $D_C = 0.05$, $K_{sp}^{het} = 111$, $K_p = 37$, $F_2'' = 2.8$, and $F_2 = 1.1$ (blue triangles) and $1.5$ (purple stars) for heterogeneous nucleation.

On the other hand, several groups have studied the modification of glassy materials by irradiation with femtosecond laser pulses (see e.g. [18]–[21] for recent reviews). The main idea behind these studies is a direct modification of the optical properties, i.e. a ‘writing’ of three-dimensional patterns inside glass. Therefore, their focus is on rather strong and localized modifications of the glassy substrate. A few early papers have demonstrated and analysed the structural modifications induced by weaker irradiation [22, 23]. In addition, it has been shown experimentally that the formation of silver as well as gold nanoparticles in glassy materials can be modified by irradiation with femtosecond laser pulses [24]–[27], although the nanoparticles and their patterns have not directly been pictured in most experiments. The necessity of an annealing step and changes of the colours of the samples show that a reaction–diffusion process with precipitation is involved, since the colours are usually due to surface-plasmon resonances of the nanoparticles. However, this process has not yet been studied in detail or employed for bottom-up structuring on smaller length scales as suggested in this paper.
Nevertheless, irradiation with femtosecond laser pulses can induce structural changes and nucleation seeds in the glass so that nucleation and precipitation rates are locally increased. Therefore, the technique can be used for inducing a spatial gradient in the nucleation threshold as needed for the formation of equidistant Liesegang bands in the approach presented in this paper. It remains to be explored whether it is experimentally easier to induce a gradient in the nanoparticle nucleation threshold itself or in its local fluctuations (or, probably, in both simultaneously). The spatial resolution and accuracy of such modification techniques, however, may be rather broad (not much below 1 \( \mu m \)) if they are merely used to set the stage for the actual bottom-up structuring process rather than directly ‘writing’ three-dimensional patterns inside the glass.

In summary, we have described an iterative procedure for obtaining equidistantly spaced Liesegang bands without \textit{a priori} knowledge of the specific process parameters. The approach is based on a continuous large-scale modification of the nucleation threshold or the heterogeneity of the substrate prior to the actual reaction–diffusion process leading to the banded precipitation. We have derived the procedure from the nucleation and growth model and confirmed it in extended Monte-Carlo lattice-gas simulations. We are convinced that the procedure can be applied experimentally and is not limited to systems exactly described by the specific model. We suggest that it can be used in bottom-up material design for obtaining patterns in the direction perpendicular to a surface. The process could eventually be combined with lateral structuring techniques such as lithography or precipitate dissolution in an electric field (see e.g. [28, 29]) to obtain three-dimensional structures. Although we have restricted this paper to equidistantly spaced Liesegang bands, replacing equation (1) with an appropriately generalized ansatz and then following the same path will enable one to obtain many other patterns.

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