Commun. Comput. Phys.
doi: 10.4208/cicp.101109.020910s

Vol. 9, No. 5, pp. 1081-1093
May 2011

Enslaved Phase-Separation Fronts and Liesegang Pattern Formation

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Received 10 November 2009; Accepted (in revised version) 2 September 2010

Available online 24 December 2010

Abstract. We show that an enslaved phase-separation front moving with diffusive speeds $U=C/\sqrt{T}$ can leave alternating domains of increasing size in their wake. We find the size and spacing of these domains is identical to Liesegang patterns. For equal composition of the components we are able to predict the exact form of the pattern analytically. To our knowledge this is the first fully analytical derivation of the Liesegang laws. We also show that there is a critical value for C below which only two domains are formed. Our analytical predictions are verified by numerical simulations using a lattice Boltzmann method.

AMS subject classifications: 35B36, 65Z05, 74S30, 76T99

Key words: Liesegang, phase separation, front, reaction diffusion, pattern formation, lattice Boltzmann, Matalon-Packter.

1 Introduction to Liesegang patterns

The formation of highly ordered patterns in naturally occurring biological, chemical, and mineralogical systems has long been a subject of intense interest. The study of such pattern formation can sometimes allow deep insight into their underlying natural phenomena. In a previous paper we analyzed the dynamics of pattern formation behind a one-dimensional, slow moving (enslaved), phase-separation front. Our analysis concerned fronts moving with constant speed, and the pattern formed was a series of alternating bands of regular width and spacing [4]. We show here that a front moving with diffusive speed will form a more complex Liesegang pattern.

It was with the motivation of understanding pattern formation in simple systems that, just over one hundred years ago, R. E. Liesegang observed a highly ordered pattern of concentric rings precipitating around a drop of silver nitrate on a glass slide with a thin

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gel coating containing potassium dichromate [8]. These concentric rings are now known as Liesegang rings. The radial width and spacing of the rings increases with increasing distance from the center. Rings close to the center are narrow and tightly packed. Rings far from the center are wide and far apart. The pattern forms from the center outwards, and is stationary once visible. Several alternatives to silver nitrate and potassium dichromate in the production of Liesegang rings have been used in the literature. In general, some electrolytes A and B combine to form an insoluble precipitate D which then produces Liesegang patterns. Most recent publications use linear Liesegang patterns of bands and gaps which are produced by adding the A electrolyte to a test-tube containing the B electrolyte suspended in gel [9].

To characterize Liesegang bands or rings, they are typically numbered from the first formed to the last formed, the nth appearing at time t_n at position x_n with a width w_n. Repeated careful measurements of Liesegang patterns revealed that discrete, defect-free bands could be characterized by a set of empirical laws [6]. They are

$$\text{Time Law} \qquad x_n \propto \sqrt{t_n}, \tag{1.1a}$$

$$\text{Spacing Law} \qquad x_{n+1}/x_n = 1+p, \tag{1.1b}$$

$$\text{Width Law} \qquad x_n \propto w_n. \tag{1.1c}$$

The *time law* relates the position of the nth band with the time of its appearance. The location of subsequent bands is given by the *spacing law*, where $p>0$ is the spacing coefficient. The *width law* states that the band width is proportional to the position of the band, which is a natural result of the *spacing law* with the assumptions of mass conservation and uniform concentration of precipitate bands [7]. These laws are only considered valid for *large* n. Much attention has been paid to the phenomenological Matalon-Packter law $p=F(B_0)+G(B_0)/A_0$, which relates p to the initial concentrations A_0 and B_0 of the A and B electrolytes [2]. $F(B_0)$ and $G(B_0)$ are known to be decreasing functions of B_0, though not much else about them is known. Antal et al. [2] show that the Matalon-Packter law can be derived in limiting cases from more general expressions.

Soon after their characterization, study into the nature and cause of Liesegang patterns was prolific. For instance, a paper by Stern in 1954 makes mention of more than six hundred papers having been published on the subject by that time [10]. There were many early attempts to develop a comprehensive model of Liesegang pattern formation. However, it proved difficult to account for the wide variety and complexity of possible patterns, and many early models were eliminated by additional experiments. The complexity of Liesegang pattern formation thwarted theoretical understanding, and progress slowed. More than a century later there is currently still no generally accepted comprehensive mechanism for Liesegang pattern formation.

Current dominating theories of Liesegang pattern formation can be categorized as either an *ion-product supersaturation* theory where electrolytes combine directly into the precipitate ($A+B\to D$), or a *nucleation and growth* theory where one or more intermediate compounds form before final precipitation ($A+B\to C\to D$). A brief discussion of these models is given in the recent paper by Jahnke and Kantelhardt [7].