Wave Optics of Liesegang Rings

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Liesegang rings refract and reflect at the interface between the regions of the same gel but of different thickness. The incident and the refracted rings obey a refraction law analogous to the Snell's law of classical optics, with a reverse of the spacing coefficient being a counterpart of the refraction index. The wavelike behavior of the rings at the interface is explained by geometrical arguments derived from the Jablczynski's spacing principle, and is reproduced in numerical simulations based on a three-dimensional minimalistic version of the nucleation-growth model.

Propagation of reaction-diffusion (RD) fronts in nonuniform media has attracted considerable scientific interest [1–3], and has been studied in the contexts of heterogeneous catalysis [4–6], cellular transport and signaling [7,8], organismal development [9], disease progression [10,11], and population dynamics [12]. RD fronts traveling through chemical or spatial discontinuities change their geometries, and in some cases exhibit behaviors analogous to those of light waves in similar situations [13–16]. Here, we show that periodic precipitation patterns [Liesegang rings (LRs)] [17] traveling between media made of the same material but of different thicknesses obey a Snell-like law with the indices of refraction replaced by the inverse of the spacing coefficients of the patterns in two regions [Figs. 1(a) and 1(b)]. Refraction and reflection of LRs are explained by simple geometrical arguments, and is reproduced in numerical simulations.

LRs were generated in a continuous layer of gelatin (10% b/w) uniformly doped with 0.5% w/w potassium dichromate, $K_2Cr_2O_7$, and cast against a glass support having a step geometry. The height of the step was 230 μm, and the depth of the gelatin layer above the raised portion of the support was varied between 100 and 400 μm. In each experiment, a small (~ 1 μL) droplet of 1 M solution of $AgNO_3$ was placed onto gelatin close (2–3 mm) to the step, and the entire system was housed in a small hermetic chamber at room temperature and with relative humidity kept constant at 40%. Patterns were allowed to develop overnight, and were subsequently analyzed by optical microscopy.

When silver cations diffused from the applied droplet into gelatin, they reacted with dichromate anions therein to give a deep colored $Ag_2Cr_2O_7$ precipitate; redistribution of this precipitate within the gel gave rise to well-defined, periodic zones of precipitation [17,18]. In gel layers of uniform thickness, precipitation zones were concentric circles (rings) around a drop, and their radii x_n obeyed the so-called Jablczynski's law, $x_{n+1}/x_n = 1 + p$, where p is the spacing coefficient [19]. In our arrangement, the rings were circular only over the constant-thickness portion of the gel in the vicinity of the applied drop, and

deformed upon crossing the boundary between the gel layers of different depths. When LRs were traveling from a thinner layer into a thicker one, the curvature of the rings increased [Fig. 1(a)]; when they traveled in the opposite direction, the curvature decreased [Fig. 1(b)]. Changes in the ring geometries were accompanied by changes in p, with the spacing coefficient being larger in the deeper portion of the gel. We have recently shown [20] that for gel layers of thickness $h > 15 \mu$m p increases approximately linearly with h, and explained this effect by relating the gel thickness to effective concentration of the outer electrolyte (Ag^+) in the gel.

Transition of LR between the two portions of the gel can be quantitatively described by a relationship resembling the Snell's law of classical optics: $p_2 \sin\alpha_1 = p_1 \sin\alpha_2$, where the subscripts denote the two regions of the gel (with the convention that propagation proceeds from "1" into "2"), $p_{1,2}$ are the spacing coefficients in these regions, and the incident and refracted angles, α_1 and α_2, are defined in Fig. 1(c) ($\alpha_{1,2}$ is the angle between the normal to the interface and the normal to the ring at the interface). To derive this law of LR refraction, we begin by noting that the rings are continuous at the interface between the two regions of the gel. Physically, continuity is the consequence of the fact that the precipitate present in one region induces ring formation (nucleation and growth) in the other, and propagates continuously across the interface.

We denote the distance between two subsequent nth and $(n + 1)$th rings along the interface as d_n [Fig. 1(c)], and consider propagation from medium denoted by subscript 1 into that denoted by subscript 2. By simple trigonometry, $d_n = w_n^1 / \sin\alpha_1 = w_n^2 / \sin\alpha_2$, where $w_n^{1,2}$ denote the distances between the rings in regions 1 and 2, respectively, and α_1 is the angle of incidence and α_2, the angle of refraction of the reaction front (rings propagate from region 1 into 2). Using the Jablczynski's law in each medium ($x_{n+1}^{1,2}/x_n^{1,2} = 1 + p_{1,2}$), we approximate $w_n^{1,2}$ as $w_n^{1,2} = x_{n+1}^{1,2} - x_n^{1,2} \approx p_{1,2}x_n^{1,2}$ to obtain $\sin\alpha_1 / \sin\alpha_2 = (p_1 x_n^1)/(p_2 x_n^2)$. Finally, because $x_n^1 = x_n^2$ at the interface, $p_2 \sin\alpha_1 = p_1 \sin\alpha_2$, which is a LR counterpart of the
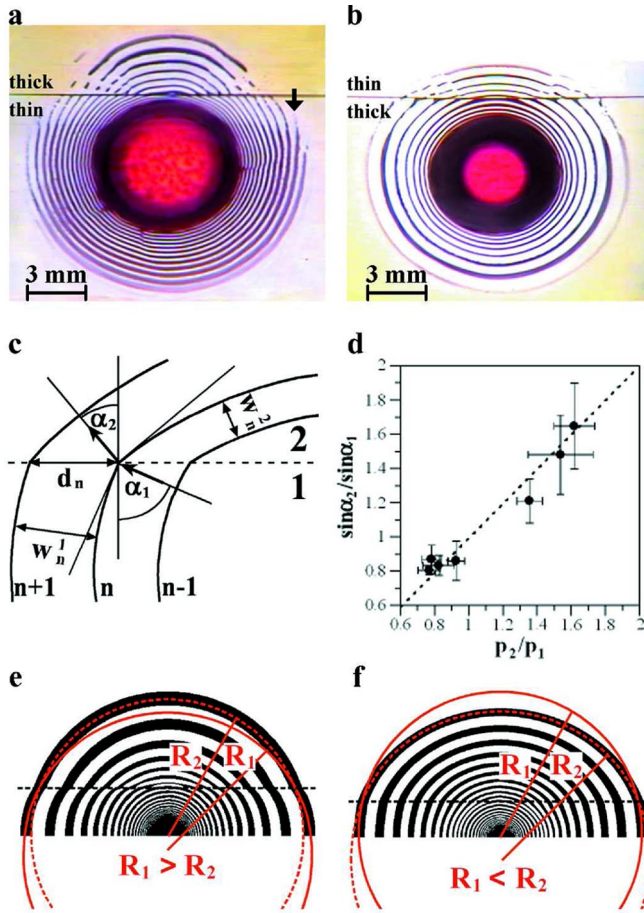
FIG. 1 (color online).　Liesegang rings forming when reaction-diffusion (RD) fronts travel between two regions of different thickness within the same gel. Dark precipitate accumulating in the rings is formed by the reaction of silver nitrate delivered from a droplet placed on the gel's surface with potassium dichromate uniformly dispersed in the gel. The picture in (a) shows a typical pattern of rings propagating from a thin into a thick layer, and that in (b) from a thick into a thin layer. The boundary between the regions is indicated by a solid line. In both cases, the incident and refracted RD fronts (rings) obey the "refraction law" analogous to the Snell's law of classical optics. The arrow in (a) indicates the ring corresponding to the critical refraction angle (see text). (c) Defines the geometry of the system. Subscripts 1 and 2 denote two regions of the gel; α_1 is the incident and α_2 the refraction angle for the nth ring crossing the interface. (d) Experimental verification of the refraction law of LRs with the measured ratios $\sin\alpha_2/\sin\alpha_1$ plotted against the ratios p_2/p_1 of the spacing coefficients. Error bars correspond to standard deviations calculated for all rings observed in a given experiment. The slope of the dashed line is unity. (e), (f) Patterns obtained in numerical simulations of the propagation of LRs across the interface separating the two portions of the gel: from a thin into a thick layer (e), and from a thick into a thin layer (f). In both cases, the relative layer thickness was 8:5 close to the typical value in the experiments. The incident and refracted LRs are sections of circles, plotted with solid and dashed lines, respectively. The radius of the circle decreases while transmitting from a shallower into a thicker layer ($R_2 < R_1$), and increases if the rings propagate in the opposite direction ($R_2 > R_1$).

Snell's law with the "indices of refraction" of the two media replaced by $1/p_{1,2}$.

Figure 1(d) shows the experimentally measured ratios $\sin\alpha_2/\sin\alpha_1$ plotted against the ratio of the spacing coefficients p_2/p_1. Each point represents an average calculated from all LRs—incident and refracted—obtained in a given experiment. As seen, the "Snell's law" is satisfied within statistical errors. The refraction law predicts that LRs originating in a deeper gel always transmit into a shallower one (since if $p_1 > p_2$, then $\alpha_1 > \alpha_2$). Propagation in the opposite direction, however, might not always be possible; this phenomenon is analogous to the optical total internal reflection. The incident rings do not physically "reflect" at the interface, but when the refraction angle, α_2, approaches the critical value, $\sin\alpha_2 = 1$, they deform in its vicinity, and do not propagate into the thicker gel region. In Fig. 1(a), the ring corresponding to the critical angle is indicated by an arrow.

The observed behavior of LRs at interfaces can be derived from the constituent RD equations. To model propagation of the rings between media of different depth, we implemented a "minimalistic" version of a three-dimensional nucleation-growth (NG) model [17,18,20,21]. (Note that in Ref. [22] three-dimensional simulations based on a kinetic Ising model was reported.) The NG model assumes that $Ag_2Cr_2O_7$ formed prior to the creation of rings is free to diffuse throughout the gel. If the local concentration of free silver dichromate (denoted henceforth $C(\mathbf{r})$, with $\mathbf{r} = (x, y, z)$) reaches some threshold value, C^*, nucleation occurs followed by aggregation into immobile precipitate, $D(\mathbf{r})$. With these assumptions, and denoting the concentration of Ag^+ cations as $A(\mathbf{r})$ and the concentration of potassium dichromate as $B(\mathbf{r})$, the NG model is written in the form of a system of three-dimensional partial differential RD equations. In dimensionless variables, $\tau = tD_A/L^2$ and $\mathbf{x} = \mathbf{r}/L$, with L being the characteristic size of the pattern, they read

$$\partial A/\partial\tau = \nabla^2 A - 2R(A, B)\theta(A^2 B - K)$$

$$\partial B/\partial\tau = D_B/D_A \nabla^2 B - R(A, B)\theta(A^2 B - K)$$

$$\partial C/\partial\tau = D_C/D_A \nabla^2 C + R(A, B)\theta(A^2 B - K)$$
$$- C\theta(C - C^\star) - CN(C, D)$$

$$\partial D/\partial\tau = C\theta(C - C^\star) + CN(C, D),$$

where K is the solubility product, and $D_{A,B,C}$ are the diffusion coefficients of A, B, and C, respectively. The step functions, θ, were used because reaction, nucleation, and aggregation are much faster than the transport of components. The step functions act here as "precipitation sinks". That is, when the argument of θ becomes positive the concentration of a given species changes instantly by an amount specified by $R(A, B)$, $N(C, D)$, or C. The function $R(A, B)$ described the kinetics of reaction and was

given by the following product $R(A, B) = \delta[c_r + (1 - c_r)r]\exp(-s^2)$. Here, δ denotes increment of the concentration of C, and is calculated from equation $(A - \delta)^2 \times (B - \delta/2) = K$. The second term in $R(A, B)$ represents the probabilistic element in the model [17], with r being a random number from an interval $[0, 1]$, and the coefficient $0 < c_r < 1$ determining the degree of stochasticity of the reaction ($c_r = 1$ and $c_r = 0$ correspond, respectively, to the fully deterministic and to fully probabilistic models). The last term follows from the stoichiometry of the reaction and the variable s is given by [17,23] $s = (2A - B)/(2A + B)$. The term $N(C, D)$ determined whether aggregation took place at a given location. The aggregation term was defined as follows: if some aggregate was already present at a given location $\boldsymbol{r}$, $D(\boldsymbol{r}) > 0$, then $N(C, D) = 1$; else, if $D(\boldsymbol{r}) = 0$ but there was some precipitate in the vicinity $\Delta\boldsymbol{r}$ of location $\boldsymbol{r}$, and if the concentration of C was above the aggregation threshold, $C(\boldsymbol{r}) > D^*$, then $N(C, D) = 1$; otherwise $N(C, D) = 0$.

The system of the RD equations was solved using the Crank-Nicholson scheme on a three-dimensional square grid. For the species B, C, and D von Neumann boundary conditions were used; the outer electrolyte, A, was subjected to von Neumann boundary conditions everywhere, except for the droplet-gel interface, where Dirichlet boundary conditions, $A(\boldsymbol{x}, \tau) = A_0$ were applied. The initial conditions were $A(\boldsymbol{x}, \tau = 0) = C(\boldsymbol{x}, \tau = 0) = D(\boldsymbol{x}, \tau = 0) = 0$, and $B(\boldsymbol{x}, \tau = 0) = B_0$. The input parameters were $A_0 = 1.0$ M, $B_0 = 0.1$ M, and $K = 10^{-11}$ [24], the ratios of the diffusion coefficients, (D_A:D_B:D_C = 1:0.06:0.04), nucleation and aggregation thresholds ($C^* = 0.08$ M, $D^* = 0.06$ M), and $c_r = 0.9$ was chosen to obtain best qualitative agreement with observed experimental patterns on gels of uniform thicknesses. Patterns obtained in numerical simulations for the LRs propagating from thin to thick and from thick to thin layers are shown in Figs. 1(e) and 1(f), respectively. In both cases, the relative layer thicknesses were 8:5. In these and other simulations, the rings refracted according to the postulated "Snell's law", with the ratios $\sin\alpha_2/\sin\alpha_1$ equal 1.20 ± 0.02 and 0.83 ± 0.03 for the rings propagating from a thin into a thick, and from a thick into a thin layer, respectively. As seen, both the incident and refracted rings are, to a good approximation, sections of circles. The radius of the circle decreases when the rings propagate from a thin into a thicker layer [Fig. 1(e)], and increases when the propagation is in the opposite direction [Fig. 1(f)].

In summary, we have shown that patterns created by periodic precipitation travel through spatial discontinuities in ways similar to their optical counterparts, and obey a Snell-like law of refraction and reflection. This work, aside from its fundamental interest, might be proven useful in microtechnology. We have recently shown [20] that arrays of microscale LRs can be created by wet stamping [25] on uniform gel surfaces, and can be used as high-quality optical elements. Knowing how the periodic precipitation patterns develop and propagate in gels of varying thickness would add more flexibility to this microfabrication technique.

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