Intrinsic instability of the concentration field in diffusion-limited growth and its effect on crystallization

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The dynamic behavior of the concentration field in crystallization is investigated by considering the coupling of the bulk concentration field and interfacial kinetics. It is shown that the concentration field may become unstable for perturbations with certain wavelength. When instability occurs, the physical environment in front of the growing interface will fluctuate and the interfacial growth mode will be affected accordingly. We suggest that our analysis can be used to interpret some spatial-temporal instabilities observed in crystallization. [S1063-651X(99)12307-9]

One of the intriguing aspects of interfacial growth is that in some cases the growth environment may become unstable spontaneously [1–9]. The instability was usually attributed to either impurity effects in interfacial kinetics [8,9], or two-dimensional (2D) nucleation and spreading of 2D islands [10,11], or some special nonlinear boundary conditions [1,2]. The physical origin of the instability, although it varies for different systems, is normally believed to associate with the competition of interfacial kinetics and chemical transportation, and nonlinear boundary conditions are sometimes required. The perturbation method is usually introduced for this type of studies. For example, Coriell and Sekerka [8] proposed an oscillatory instability related to a ''solute pump'' mechanism, according to which the local changes in segregation coefficient k originated from the periodic changes in the interfacial velocity v can occur out of phase with local interface position. This leads to lateral inhomogeneity of concentration on a length scale large enough that the resulting instabilities will not be suppressed by capillarity. Moreover, the effect of anisotropic kinetics on morphological stability of a pure material growing at constant velocity into a supercooled melt was investigated by Chernov, Coriell and Murray [12]. Although great efforts have been devoted to this type of problem, however, it seems that many questions remain open. One of these is whether the oscillatory behavior of the concentration field could be an intrinsic property of the diffusion-limited growth. In this paper, starting from conventional diffusion equation and boundary conditions [13], we show that both the bulk solute concentration at the interface and the interfacial concentration of adsorption molecules may become unstable for perturbations with certain wavelength, which might be the origin of some spatial-temporal oscillations in the interfacial growth.

Following Gilmer, Ghez, and Cabrera [13], crystal growth from an aqueous solution can be modeled as the following: (i) solute molecules diffuse through supersaturated volume to growing interface, (ii) solute molecules exchange between the volume near the surface and the close-packed terraces where molecules are adsorbed, and (iii) adsorbed molecules diffuse on the terraces in between steps and incorporate into kink sites on the steps. In this model direct incorporation of solute molecules by volume diffusion is not considered. We suppose that the adsorption molecules on the interface have an average lifetime τ, beyond which the molecules will desorb from the interface and go back to the volume.

A two-dimensional model is taken, where the interface grows in a $+y$ direction. The volume concentration field $C(x,y,t)$ and the interfacial adsorption concentration field $n_s(x,t)$ are considered. The volume concentration field $C(x,y,t)$ satisfies

$$\frac{\partial C(x,y,t)}{\partial t}=D_v\left(\frac{\partial^2 C(x,y,t)}{\partial x^2}+\frac{\partial^2 C(x,y,t)}{\partial y^2}\right), \quad (1)$$

where D_v is the volume diffusion coefficient. In the vicinity of growing interface ($y\in\varepsilon$ and $\varepsilon\rightarrow0$) the concentration fields obey the following relation:

$$D_v\frac{\partial C(x,y,t)}{\partial y}\bigg|_{y\in\varepsilon}=\frac{D_v}{\Lambda}C(x,y,t)\bigg|_{y\in\varepsilon}-\frac{n_s(x,t)}{\tau}, \quad (2)$$

where Λ is a phenomenological coefficient describing the kinetics of particle exchange between the volume and the adsorbed layer [13]. At the crystal surface, mass conservation requires

$$j_v=\nabla\cdot j_s+\frac{dn_s(x,t)}{dt}, \quad (3)$$

where the mass flux from volume $j_v=-D_v\partial C(x,y,t)/\partial y|_{y\in\varepsilon}$ and the surface mass flux $j_s=-D_s\nabla n_s$, D_s is the surface diffusion coefficient. Both D_v and D_s are taken as constant. The growth rate of the crystal surface depends on the diffusion flux of adsorption molecules towards the steps, while this flux is determined by local adsorption concentration gradient on the step sites.

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The analytical solutions of the coupled equations (1) and (3) with boundary conditions discussed in Ref. [13] are not easy to get, although the stationary solutions are known. The stationary solutions of these two equations can be obtained as

$$C(x,0)=(1+\sigma)C_0-\frac{qb\lambda}{lD_v\tau}\left[\frac{\delta}{\lambda}+2\sum_{k=1}^{\infty}\frac{\tanh\left(\frac{2\pi k}{l}\delta\right)\cos\left(\frac{2\pi kx}{l}\right)}{\frac{2\pi k\lambda}{l}\left[\left(\frac{2\pi k\lambda}{l}\right)^2+b\frac{2\pi k\lambda}{l}\tanh\left(\frac{2\pi k\delta}{l}\right)+1\right]}\right],$$

$$n_s(x)=(1+\sigma)\frac{D_v\tau C_0}{\Lambda}-\frac{q\lambda}{l\Lambda}\left[1+\frac{\delta}{\lambda}b+2\sum_{k=1}^{\infty}\frac{\left[\frac{2\pi k\lambda}{l}+b\tanh\left(\frac{2\pi k}{l}\delta\right)\right]\cos\left(\frac{2\pi kx}{l}\right)}{\frac{2\pi k\lambda}{l}\left[\left(\frac{2\pi k\lambda}{l}\right)^2+b\frac{2\pi k\lambda}{l}\tanh\left(\frac{2\pi k\delta}{l}\right)+1\right]}\right],$$

$$q=D_v\tau\sigma C_0\left[\frac{\Lambda_s}{\lambda}+\frac{\lambda}{l}\left(1+\frac{\delta}{\lambda}b+2\sum_{k=1}^{\infty}\frac{\frac{2\pi k\lambda}{l}+b\tanh\left(\frac{2\pi k}{l}\delta\right)}{\frac{2\pi k\lambda}{l}\left[\left(\frac{2\pi k\lambda}{l}\right)^2+b\frac{2\pi k\lambda}{l}\tanh\left(\frac{2\pi k\delta}{l}\right)+1\right]}\right)\right]^{-1},$$

where σ defines the supersaturation, C_0 is the equilibrium concentration at the temperature of crystal growth, b is the interstep distance, l represents the thickness of the boundary layer, δ is the thickness of the unstirred boundary layer, λ is the mean diffusion distance, which obeys $\lambda^2=D_s\tau$, and Λ_s is a coefficient describing the kinetics of particle exchange between the step and the adsorbed layer. Detail deduction has been given in Ref. [13]. Even so, we are able to survey the stability of $C(x,y,t)$ and $n_s(x,t)$. From Eqs. (1)–(3), a coupled equation of the adsorption concentration field and the volume concentration field in the vicinity of growing interface is derived:

$$\frac{dn_s(x,t)}{dt}=\frac{D_v}{\Lambda}C(x,y,t)\bigg|_{y\in\varepsilon}-\frac{n_s(x,t)}{\tau}+D_s\frac{\partial^2 n_s(x,t)}{\partial x^2}. \tag{4}$$

We are particularly interested in the stability of $C(x,y,t)|_{y\in\varepsilon}$ and $n_s(x,t)$, because they influence the interfacial growth significantly. The second order derivative of volume concentration near the interface can be derived from Eq. (2) as

$$D_v\frac{\partial^2 C(x,y,t)}{\partial y^2}\bigg|_{y\in\varepsilon}=\frac{\partial}{\partial y}\left(D_v\frac{\partial C(x,y,t)}{\partial y}\right)\bigg|_{y\in\varepsilon}$$

$$=\frac{D_v}{\Lambda}\frac{\partial C(x,y,t)}{\partial y}\bigg|_{y\in\varepsilon}$$

$$=\frac{1}{\Lambda}\left(\frac{D_v}{\Lambda}C(x,y,t)\bigg|_{y\in\varepsilon}-\frac{n_s(x,t)}{\tau}\right). \tag{5}$$

Substituting Eq. (5) into Eq. (1), an equation of volume concentration in the vicinity of growing interface is obtained:

$$\frac{\partial C(x,y,t)}{\partial t}\bigg|_{y\in\varepsilon}=D_v\frac{\partial^2 C(x,y,t)}{\partial x^2}\bigg|_{y\in\varepsilon}+\frac{D_v}{\Lambda^2}C(x,y,t)\bigg|_{y\in\varepsilon}$$

$$-\frac{n_s(x,t)}{\Lambda\tau}. \tag{6}$$

Based on Eqs. (4) and (6), a linear stability analysis is applied. We introduce plane-wave perturbations to the concentration fields at the growing interface. The perturbed concentration fields are assumed to have the form of

$$n_s^p(x,t)=n_s(x,t)+\tilde{n}_s e^{\omega t}e^{-ikx}, \tag{7}$$

$$C^p(x,y,t)|_{y\in\varepsilon}=C(x,y,t)|_{y\in\varepsilon}+\tilde{C}e^{\omega t}e^{-ikx}.$$

Taking the perturbed solutions (7) into Eqs. (4) and (6), a dispersion equation is achieved,

$$\omega^2+\left[\frac{1}{\tau}-\frac{D_v}{\Lambda^2}+k^2(D_v+D_s)\right]\omega+\left(D_sk^2+\frac{1}{\tau}\right)\left(D_vk^2-\frac{D_v}{\Lambda^2}\right)$$

$$+\frac{D_v}{\Lambda^2\tau}=0. \tag{8}$$

The dynamic behavior of interfacial concentration fields depends on the property of ω. When the wave vector k is in the range

$$\frac{\sqrt{\frac{D_v}{\Lambda^2}}-\sqrt{\frac{1}{\tau}}}{\sqrt{D_v-D_s}}<|k|<\frac{\sqrt{\frac{D_v}{\Lambda^2}}+\sqrt{\frac{1}{\tau}}}{\sqrt{D_v-D_s}}, \tag{9}$$
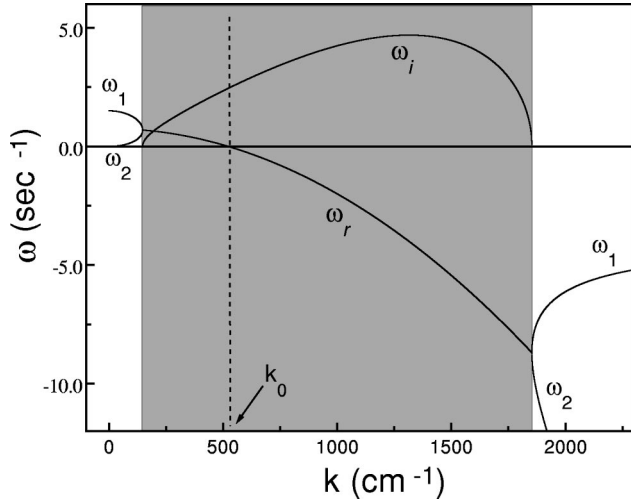
FIG. 1. The dispersion relation to show the dependence of ω on the wave vector k. In the shaded region ω is complex, where the real and the imaginary parts are denoted as ω_r and ω_i, respectively. Beyond the shaded region, ω has two real solutions marked as ω_1 and ω_2. The dashed line marks the marginal state with $\omega_r=0$, where $k=k_0$. The parameters to make the plot are $D_v=5.5\times10^{-6}$ cm^2/s, $D_s=1.0\times10^{-9}$ cm^2/s, $\tau=0.25$ s, $\Lambda=1.0\times10^{-3}$ cm.

ω is complex and oscillatory behavior is expected. However, whether such oscillatory instability is eventually observable depends on the sign of the real part of ω, ω_r. If ω_r is always negative, instability decays exponentially and the perturbation eventually vanishes. In this case the concentration field is stabilized. If ω_r becomes positive beyond a certain k, perturbation amplitude of the interfacial concentration field approaches infinite as time goes on and thus instability occurs. The turning point of these two scenarios is a marginal state with $\omega_r=0$, which corresponds to a sustained periodic oscillation of the interfacial concentration field. The wave vector of this marginal state is

$$k_0=\sqrt{\dfrac{\dfrac{D_v}{\Lambda^2}-\dfrac{1}{\tau}}{D_v+D_s}}. \qquad (10)$$

We plot in Fig. 1 the dispersion relation $\omega(k)$. In the shaded region, k satisfies Eq. (9) and ω has an imaginary part ω_i and a real part ω_r. While in the other regions, two real solutions exist, which are denoted as ω_1 and ω_2, respectively. The dashed line marks k_0. Figure 1 suggests that the growth system will selectively respond to the perturbations with different wavelength. When the wave vector of perturbation is greater than k_0, the perturbation is damped and the concentration fields are stabilized; when the wave vector of perturbation is smaller than k_0, however, the perturbation amplitudes of concentration fields may either fluctuate in a complicated way, or increase exponentially. Consequently, instability is expected in the crystal growth. In this case, nevertheless, the detail dynamic behavior of the unstable concentration fields is beyond the capability of the perturbation method. Instead of studying the complicated unstable scenario, we focus on the marginal stable oscillatory state with $\omega_r=0$. Meanwhile the temporal oscillation period,

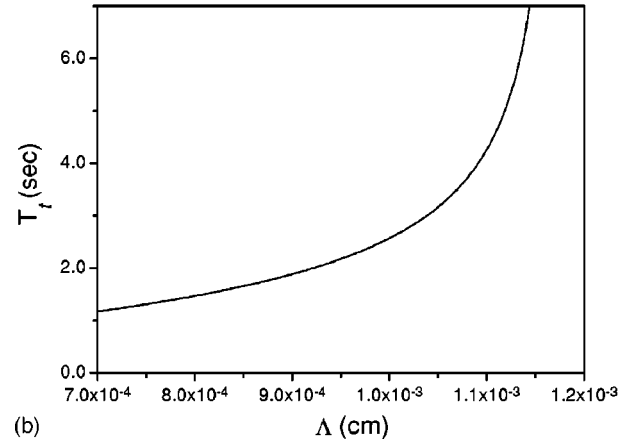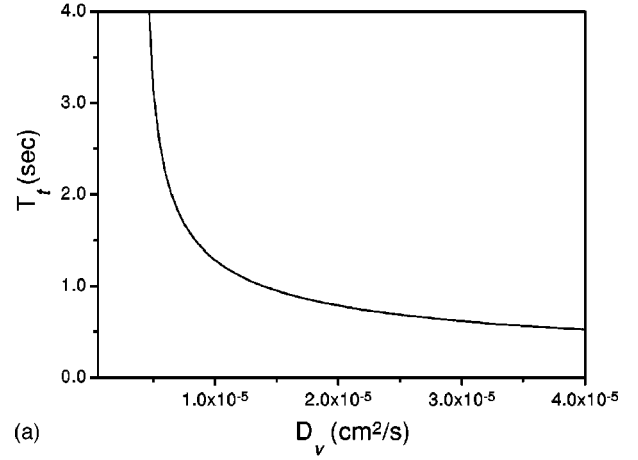

FIG. 2. (a) The relation of the temporal oscillation period T_t and the volume diffusion coefficient D_v. The parameters are selected as $D_s=1.0\times10^{-9}$ cm^2/s, $\tau=0.25$ s, and $\Lambda=1.0\times10^{-3}$cm. (b) The temporal oscillation period T_t as a function of Λ. The parameters to make the plot are $D_v=5.5\times10^{-6}$ cm^2/s, $D_s=1.0\times10^{-9}$ cm^2/s, and $\tau=0.25$ s.

$T_t(=2\pi/\omega_i)$, is a function of D_v, D_s, Λ, and τ. Figure 2(a) shows the relation of T_t and the volume diffusion coefficient D_v. The oscillation period decreases as D_v increases. In order to observe the oscillation of the interfacial concentration field, the volume diffusion coefficient should be of proper value, so that the oscillation period is not too long or too short. Figure 2(b) illustrates the temporal oscillation period T_t as a function of Λ. T_t increases dramatically when Λ is larger than a certain value. It is known that Λ relates to the activation energy barrier for surface adsorption, ΔU_{ad}, as $\Lambda\propto\exp(\Delta U_{ad}/kT)$ [13], where k is Boltzmann constant and T is temperature. A larger Λ corresponds to a higher ΔU_{ad}. For sufficiently high energy barrier ΔU_{ad} the chance of surface adsorption drops significantly and the effective supply flux from volume decreases. As a result, the period of temporal oscillation increases. In Fig. 3(a), we plot $\omega_r(k)$ for different volume diffusion coefficient D_v. When D_v becomes less than a certain value, ω_r is always negative and the concentration field is stabilized. Figure 3(a) suggests that instability takes place more easily for long wavelength perturbations when the volume diffusion coefficient is higher, which is consistent with previous studies [12]. Figure 3(b) demonstrates $\omega_r(k)$ at different surface diffusion coefficients.
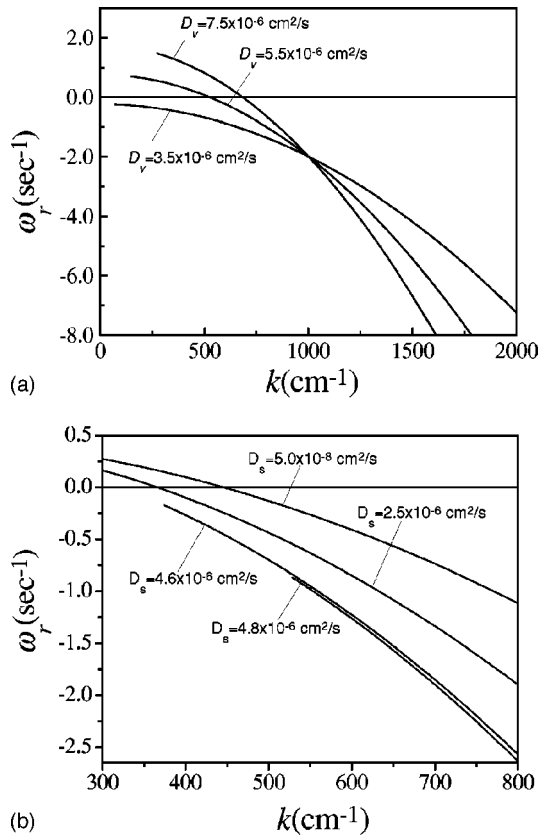
FIG. 3. (a) The curve of $\omega_r(k)$ for different volume diffusion coefficients D_v in the region where $\omega(k)$ has a complex value. It can be seen that for sufficiently low D_v, ω_r is always negative and the concentration field is stabilized. The parameters to make the plot are $D_s = 1.0 \times 10^{-9}$ cm²/s, $\tau = 0.25$ s, and $\Lambda = 1.0 \times 10^{-3}$ cm. (b) The plot to show the dependence of $\omega_r(k)$ on surface diffusion coefficient D_s. $\omega_r(k)$ is always negative when the surface diffusion coefficient is sufficiently high (meanwhile, D_s becomes comparable to D_v). This means that for a specific growth system, faster surface diffusion stabilizes the interfacial concentration field. The parameters to make this plot are $D_v = 5.0 \times 10^{-6}$ cm²/s, $\tau = 0.25$ s, and $\Lambda = 1.0 \times 10^{-3}$ cm.

It follows that $\omega_r(k)$ becomes negative for sufficiently large D_s. The negative $\omega_r(k)$ means that the perturbation to the concentration field will finally be damped. So Fig. 3(b) indicates that faster surface diffusion stabilizes the interfacial concentration field. In this case, the chance for the adsorption molecules to reach kink sites on the step becomes much higher. Once the molecules incorporate into the kink sites they are considered as a part of the crystal. Therefore, the interfacial growth, which acts as the drain of adsorption molecules, becomes faster for higher D_s. When the drain of adsorption molecules turns strong enough, the interfacial concentration field will no longer oscillate.

We suggest that the instability of the concentration field at growing interface originates from the competition of nutrient transport and interfacial kinetics. With a fixed volume supply, adsorption concentration will not be accumulated when the lifetime of adsorption τ drops (i.e., the adsorbed molecules jump back to the volume easily), or the surface diffusivity becomes very high. To some extent, this situation is similar to that of the Lotka-Volterra model (or, predator-prey

model) in ecosystem [14]. In a solution growth system, it is generally accepted that the volume diffusion coefficient D_v is much larger than that of surface diffusion, D_s [15]. Figure 3(b) implies that a large difference between D_v and D_s is required to observe oscillatory instability of the interfacial concentration field. Due to the fact that D_v is significantly larger than D_s for many solution growth systems, in these systems the dynamic behavior of the concentration field is essentially determined by the volume diffusion, the interfacial adsorption, and desorption.

The unstable interfacial concentration field and its effect on crystallization have been observed in several growth systems. In electrocrystallization, periodic oscillation of the concentration field was visualized by differential interference contrast microscopy and was related to the sidebranching of dendrites [4]. For crystal growth from a thin aqueous solution film with a free surface, periodic change of surface-tension gradient originated from the concentration oscillation, together with a wetting effect of aqueous solution film on the substrate, finally leads to a periodic variation of interfacial growth rate [3]. Furthermore, unstable interfacial growth was observed by Vekilov, Alexander, and Rosenberger [5] in the crystallization of lysozyme, and by Tsukamoto et al. [16] in the growth of $Ba(NO_3)_2$ from a convection-free environment. If the instability of the interfacial concentration field takes place near the critical value for kinetic roughening transition, one would expect an alternating change of interfacial growth mode between a faceted one and a rough one. Our recent studies on the surface morphology of the aggregate of NH_4Cl crystallites [6] seems to support this speculation.

As we reported previously [6], crystallites of NH_4Cl in an agarose gel growth system can form a fractal-like aggregate on the glass substrate. Viewed under optical microscope, the surface of crystallites is completely rough in the early stage of growth when the initial concentration of NH_4Cl is above 10%. As crystal growth proceeds, faceting takes place locally over the rough, rounded surface of the aggregates, which is characterized by the bunching of steps and the generation of 2D islands. In between two regions of faceted growth, the surface of crystallites remains rough. In this way an alternating change of faceted growth and rough growth takes place. It is true that the spatial distribution of the regions of rough and faceted growth is not exactly periodic. However, fluctuation of the spatial period is not significant. Therefore, we are still able to define an average spatial period of the roughening transitions. By changing agarose concentration in preparing the gel medium, the effective volume diffusion coefficient is modified. Although we do not know the quantitative relation of the volume diffusion coefficient of NH_4Cl with respect to agarose concentration (or, the density of the gel medium), it is reasonable to assume that the effective volume diffusion coefficient decreases when the agarose concentration is increased. We measured the average spatial period of the alternating roughening transitions over the surface of aggregate as a function of the concentration of agarose. It was found that the spatial period is shortened when the gel concentration is decreased [6]. This experimental observation can be explained by our model. Suppose that we have a moving frame of coordinates fixed on the growing tip of an aggregate branch. In addition, local interfacial concen-

tration is initially higher than the critical concentration for a kinetic roughening transition. Meanwhile the surface of crystallites is roughened. When instability occurs, the local concentration field in front of the growing interface fluctuates and it may become lower than the critical concentration for kinetic roughening. Once this occurs, the nucleation rate decreases considerably and the growing interface changes to a faceted one. When the aggregate branch moves forward, as soon as the local concentration in front of the growing interface fluctuates higher than the critical value for a kinetic roughening transition, rough crystal growth reappears. In this way, the temporal fluctuation of interfacial concentration field in the moving frame of coordinates results in the spatial alternating roughening transitions over the surface of aggregate branches. Figure 2(a) indicates that the temporal oscillation period is shortened when the volume diffusion coefficient is increased. In other words, by decreasing the agarose concentration, the temporal oscillation period is shortened. Suppose the tip growth rate remains a constant during the roughening transition process; it follows that the spatial period of the roughening transition should decrease at lower agarose concentration, which is consistent with our experimental observation [6].

It should be mentioned that in many previous studies, oscillatory spatial and temporal processes were attributed to the chemical impurities on the growing interface [8,9,17] or the asymmetry in attachment kinetics on the crystal surface [18,19]. It was also argued that the unsteady growth may be due to a highly nonlinear response of the system that results in a mixed control regime from the coupling of solute bulk transport with nonlinear interfacial kinetics [5]. Indeed these factors can be responsible for the unstable growth; however, our results suggest that the instability of interfacial concentration fields and interfacial growth could be an intrinsic behavior of diffusion-limited growth itself. Furthermore, oscillatory dynamic behavior is not restricted to crystallization only. As a matter of fact, many spatiotemporal oscillations have been observed in reaction-limited interfacial processes and in catalysis systems [20,21]. Due to the generality of the equations presented in this paper, we expect that our analysis should also be applicable to these systems.

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