Growth dynamics of nanoplatelet liquid crystals by directionally drying colloidal suspensions in a confined channel

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ABSTRACT

Unidirectional solvent evaporation has been increasingly concerned as a versatile microfluidic agent in manipulating the self-assembly dynamics of shape anisotropic colloids by precisely governing a confined nanofluid flow in a microcell. Here we develop a theoretical framework upon unidirectional drying-induced growth of nematic liquid crystals (LC) in nanoplatelet suspension confined to a Hele–Shaw (H–S) channel. The nematic order-dependent permeability assembled in modified Darcy's law and the interactions between nanoplatelets for nematic LC are both explicitly incorporated in a confined nanofluid flow. The growth dynamics of nematic LC that is highly correlated with drying rate (drying Peclet number), nanoplatelet aspect ratio, and geometric confinement have been rationalized by our numerical measurements. Unlike the spherical colloids, the nematic LC grows nonlinearly over time indicating a time-dependent instantaneous growth velocity. The final length of LC, when subjected to an enhanced drying rate, is seen to be compressed toward the drying end, but its time-averaged growth velocity increases significantly. Besides, the LC formed by the thicker nanoplatelets gets the shorter final length, while whether its average growth velocity is affected by nanoplatelet types depends on the drying rate. Importantly, we confirm a noticeable promotion in the growth of LC as the enhanced geometric confinement is imposed. A state diagram we produce suggests a universal signature of enhancement in solvent drying flux with enhanced confinement. However, our results highlight the favorable water retention in nanoplatelet nematic LC with compacted layered architecture prevailing over the spherical colloids deposits with the porous percolation architecture.

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I. INTRODUCTION

Drying suspensions containing the insoluble solutes, for instance, micro- and nanoparticles, polymers, and proteins, have been widely employed as a versatile approach to manipulate the collective transport processes of the solutes. Accordingly, pattern formations, rich phase behaviors, and self-assembly in advanced soft materials can be precisely engineered.^{1–4} Experimentally, the drying processes can be performed via two different manners, such as a vertical drying, i.e., drying colloidal or polymeric droplets and thin films on an open-type flat substrate,^{5–7} and a lateral (unidirectional) drying, i.e., the aqueous suspensions are dried in the geometric confined channel, like a Hele–Shaw (H–S) cell.^{8–13}

The directional accumulation of these insoluble solutes driven by solvent evaporation always leads to the dense particulate packing domain where the resulting deposition patterns can form with morphologies. For instance, the ring-like morphologies including coffeering, multiple-concentric rings, even fractal-like rings for the vertical dryings,^{3,4,14,15} and the formations of polygonal arrangement,¹² heat flux-driven orderly pattern of nanoparticles,¹⁶ parallel array cracks,^{8,17-20} and even shear banding^{21,22} for the unidirectional dryings. Although some resemblances exist, the unidirectional dryings can be much more versatile than the vertical (open-type) dryings in characterizing how a colloidal/polymeric solution changes continuously from liquid to solid when drying. Naturally, the unidirectional dryings achieve enormously broad range of industrial applications and scientific interests, such as coatings and adhesives,^{23,24} directional solidification,^{11,25-28} and also guidance in engineering micro/nano-crystals growth, 12,19 and microfabrication of thin films. $^{29-31}$ In a directional drying protocol, a liquid film or a droplet is sandwiched between two glass slides, i.e., confined inside an H-S channel, and dried in one side as termed by the drying end, while the opposite side is an open-free end containing a liquid-air interface. As the drying proceeds, the evaporating water (or the volatile solvent) will create a viscous flow of bulk suspension with carrying the micro/nanoparticles

(colloids or polymers) toward the drying end. As time goes on, the significant concentration gradient emerges such that three state domains can be observed, including the dense packing domain at the drying end, followed by the LST domain, and the reservoir domain far away from the drying end.^{11,12,27–31}

As is well known, the drying behavior is a representative *out-of-equilibrium* pathway associated with the viscous fluid dynamics and the transport dynamics of (micro/nano) particulate matter. The descriptions of dynamics in directional drying of the colloidal/ polymeric suspensions in a (micro) H–S channel have been presented experimentally and theoretically.^{12,13,24–31} Previously, the suspensions consisted of spherical colloids are frequently employed in probing the rich drying behaviors. For example, several studies have experimentally demonstrated the observations of disorder-to-order (hexagonal arrangement) phase transition, ^{5,12,19} as well as the occurrence of structural anisotropy,²⁷ in the packing deposits of spherical colloids by lateral dryings. Moreover, a systematic examination of the multifactor and the effectiveness in regulating the formation kinetics of local cracks and the crystallinity in dense deposits of colloidal spheres have also been implemented by the recent experiments.¹²

However, the case becomes strikingly different when the dispersed micro/nanoparticles are non-spherical. The anisometric colloidal particles, such as rod-like and platelet-like particles, noticeably distinguish from the spherical particles due to their phase transition from isotropic (I) phase to anisotropic phase as the particle concentration increases over a threshold value.^{32–37} Such a phase transition is indicative of the resulting liquid crystals that usually form in the dense deposit domain. As a matter of fact, the crystallization of the spherical colloids only appears with the polygonal configurations in space arrangement. Instead, the anisometric particles show rich ordered crystalline phases, known as nematic (N) phase, columnar (C) phase, and smectic (S) phase, owing to their additionally orientational degree of freedom in the alignment configurations. The crystallization processes between the spherical and the anisometric colloids are therefore intrinsically different. Theoretically, the physical landscape in phase transition of the anisometric colloids at thermodynamic equilibrium has been well clarified by several groups,^{33–35} after much pioneering work by Onsager.³² Experimentally, sedimentation prevails as a longstanding pathway in conducting the observations of growth kinetics of the liquid crystals, and also testifying those proposed theories on phase behaviors, while it is time-consuming and unmanageable.

Alternatively, as mentioned above, the evaporating solvent is able to act as a competent strategy to create a large concentration gradient, in consequence, the structural self-assembly configurations of solutes can be modulated more desirably with varied concentrations. Besides, the concentration threshold triggering the liquid crystalline phase transition for the anisometric colloids is much lower than that for the spherical colloids. This suggests that solvent evaporation is a more effective pathway to manage the growth of liquid crystals of nonspherical colloids. Some paradigms have existed in vertical drying of suspensions with dispersed rod-like particles. Dugyala and Basavaraj presented an experimental study of drying sessile droplets containing silica rods and elucidated the conditions of how order-disorder phase transition is arranged in the accompanying ring deposit.⁷ Lebovka et al. implemented kinetic Monte Carlo simulations on studying the vertical drying of a colloidal film containing rod-like particles, and the dependences of orientation-based self-assembly and stratification of

the rods on the evaporation rate and the concentration have been discussed.^{38,39} Nonetheless, the investigations associated with unidirectional drying of the anisometric colloid suspensions, especially for the colloidal platelets, confined in an H–S channel have until recently remained largely unexplored in either experiments or theories.

In this work, we shall present a theoretical framework for the dynamics in unidirectionally drying a suspension containing the colloidal platelets in a geometric confinement H-S channel. Our continuous model was derived on the basis of non-equilibrium transport equation of solutes with coupling to the viscous nanofluid flow confined to an H-S channel. The orientation-dependent permeability in the modified Darcy's law for resulting nanoplatelet nematic crystals and the interactions between the nanoplatelets based on the exclusion volume theory has been precisely taken into account. Our results identify the existence of three-phase configurations with varied concentrations of nanoplatelets, ranging from the drying end toward the liquid-air interface, termed as nematic phase domain, subconcentrated phase in the liquid-solid transition (LST) domain, and isotropic phase in the reservoir domain. We show that the LST domain is formed first followed by the formation of nematic phase domain with higher nanoplatelet concentration at the drying end. The fronts of these two domains are shown to move backward together at different velocities in the H-S channel. The growth of nanoplatelet liquid crystals (the nematic phase) as specified by the receding N phase front is found to be nonlinearly time-dependent throughout the drying, which strikingly differs from the growth behavior of deposit film packed by spherical colloids.¹³ We demonstrate that the drying behaviors of the nanoplatelet suspension, as well as the growing liquid crystals, are highly susceptible to the drying rate (Peclet number), the nanoplatelet aspect ratio, and the geometric confinement of H-S channel. The influences of all these factors will be rationalized in this work.

Figures 1(a)-1(c) show the schematic illustrations for the directional drying system, a cross-section guidance of the H–S channel to



FIG. 1. (a) Schematic illustration of directional drying system. (b) Cross-section sketch illustrating the migration of colloidal platelets guided by the red arrows, resulting phase configurations in different domains, and the coordinate system. The nematic phase front and the LST front both recede inwards in H–S channel guided by the black arrows, and the liquid–air interface at the open end moves toward the drying end due to drying flux guided by the gray arrow. (c) Model of a colloidal platelet as specified by its diameter 2a, thickness 2b, and the orientational order in the resulting nematic phase as shown in (b).

identify the resulting multi-phase transition domains, and the nanoplatelet model, respectively. It is also worth mentioning that though the experiments available for the present problem with respect to the nanoplatelets still await, an interesting experiment to manipulate the directional migration of the ZrP nanoplatelets in a confined rectangular cell using temperature gradients has been recently reported by Shinde *et al.*⁴⁰ Their direct experimental observations, as illustrated in Fig. 2(b), help qualitatively access the drying scenario of nanoplatelet suspension we will discuss in this work.

II. THEORETICAL DESCRIPTIONS

In the drying system, we assume that the colloidal platelets are monodispersed in the suspension with the volume fraction ϕ (actually the colloidal platelets are usually polydisperse in the suspensions,²¹ while such a size polydispersity can be definitely controlled less than 0.2 in the experiments,^{11,12,40} so that the current assumption of monodispersed nanoplatelets could be sound). The suspension film is initially homogenous with nanoplatelets loading ϕ_0 , and dried in a H–S channel with an initial length L_0 . As seen in Fig. 1(c), the nanoplatelet is modeled as a thin discotic particle with diameter 2a and thickness 2b. The volume and aspect ratio of a nanoplatelet are $\sigma = 2\pi ba^2$ and $\lambda = a/b$, respectively. We set up coordinate system as shown in Fig. 1(b), and the direction of suspension flow due to the directional drying of water is opposite to x-axis direction. Let v_s , v_p and v_f are the volume-averaged velocities of the bulk medium, the nanoplatelet, and the water, respectively. We then naturally define the following relationship:

$$v_s = \phi v_p + (1 - \phi) v_f. \tag{1}$$

In the directional drying protocol, only water (solvent) can be dried out of the channel, thus the average velocity of water evaporation v_f that is measured as the drying flux in experiments can function as a proxy for the average evaporation rate in a drying system.^{13,30,31} Here,

we assume a uniform drying rate, i.e., the velocity v_f is a constant, for simplicity.

During the drying, the conservation law of the colloidal platelets is given by

$$\dot{\phi} = -\frac{\partial \phi v_p}{\partial x} = -v_f \frac{\partial \phi}{\partial x} - \frac{\partial v_s}{\partial x}.$$
(2)

In Eq. (2), the bulk suspension velocity v_s is unknown and should be determined by considering the viscous flow of nanofluid confined to the H–S channel with a low Reynolds number. In this study, the momentum balance for the bulk nanofluid can be represented as

$$\eta(\phi)\frac{\partial^2 v_s}{\partial z^2} = \nabla P,\tag{3}$$

where $\eta(\phi)$ is the viscosity of colloidal suspension that is usually correlated with the colloids concentration. Equation (3) is in fact equivalent to the steady state Stokes equation for a nanofluid which has inhomogeneous concentration distribution of nanoplatelets. Hereby, the total pressure *P* in Eq. (3) for the colloidal platelet suspension can be decomposed as $P = p + \Pi$, where *p* is the hydrostatic pressure from the fluid phase, and Π is the osmotic pressure due to the dispersed nanoplatelets.¹¹ The velocity v_s in Eq. (3) can be calculated by adopting the no-slip boundary condition in H–S channel, $v_s(z = 0)$ $= v_s(z = H) = 0$. To simplify the problem into 1-D flow configuration, we employ a volume-averaged form of v_s along *z*-axis, yielding

$$v_s = -\frac{H^2}{12\eta(\phi)} \left(\frac{dp}{dx} + \frac{\partial\Pi}{\partial x}\right). \tag{4}$$

The rheology in colloidal suspensions is often dependent on concentration and has been characterized by the Einstein–Batchelor theory or various (semi) empirical expressions for the dilute case. The molecular dynamic simulations have suggested a simple formula to describe this



FIG. 2. (a) Phase diagram showing I–N phase transition of the colloidal platelets at thermodynamics equilibrium state. The arrows guide eyes on the transition concentration threshold ϕ_{I-N} . The inset in (a) shows the TEM image of ZrP nanoplatelets [Reproduced with permission from Li *et al.*, Phys. Rev. E **90**, 020504 (2014). Copyright 2014 American Physical Society].⁴⁷ (b) The experimental paradigm on manipulating directional growth of ZrP nanoplatelets liquid crystals in a confined rectangular cell using temperature gradients as reported by Shinde *et al.* [Reproduced with permission from Shinde *et al.*, ACS Nano **13**, 12461–12469 (2019). Copyright 2019 American Chemical Society].⁴⁰ The direct observations in the graphs approximately represents the similar dynamics process of the growing nanoplatelet nematic phase in a H–S channel by drying as discussed here. The bright phases are the nanoplate nematic liquid crystals.

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rheological property well, $\eta(\phi) = \eta_0 (1 + A_1 \phi + A_2 \phi^2)$, where η_0 is the constant of solvent viscosity, and the coefficients A_1 and A_2 are highly sensitive to the nanoparticle shape, and we adapt here the estimations for the nanoplatelets suggested by Timofeeva *et al.*⁴¹

In Eq. (4), the osmotic pressure gradient actually implies the drag friction felt by the nanoplatelets due to the relative motion between the nanoplatelet and the bulk medium. The determination of the hydrostatic pressure gradient in Eq. (4), however, is vital but somehow always controversial.¹¹ Here, we argue that for the colloidal platelet dispersions the hydrostatic pressure drop in the bulk fluid can be accounted for the capillary-driven flow.¹³ As stated earlier, as the drying proceeds, a dense solid-like deposit can form with a resulting nematic phase configuration of the arrested nanoplatelets at the drying end, as a result, a capillary pressure drop will emerge when the evaporating solvent is forced to flow throughout such a structural deposit regime. The capillary-driven flow is qualified here by Darcy's law, reading as $\nabla p = -\frac{\eta_0}{\kappa(\phi)}(1-\phi)(v_f - v_p)$, where $\kappa(\phi, s)$ is the permeability in the nano-suspension as a function of nanoplatelet concentration and the order parameter. Such a permeability function in the mixture of solvent (continuous phase) and dispersed particle (discrete phase) is hard to be determined strictly, in particular for the anisometric colloids. Several (semi) empirical formulas of $\kappa(\phi)$ have been proposed by fitting the experimental measurements, for instance, Carmen-Kozeny expression and Russel expression for hard sphere system, which suggest a simple scaling law as $\kappa(\phi) \sim A(\phi)r^2$ with r being radius of the spherical particle and $A(\phi)$ a hindrance function.^{42,43} The case for platelet-like particle, however, can be more complicated because its large aspect ratio and the nature of reoriented alignment affecting the permeability significantly. For example, when the orientation of nanoplatelets in the nematic phase is perpendicular to their diffusion direction, the solvent percolation throughout such a nematic layer is extremely lowered; instead, if this orientation is parallel to their diffusion direction, the solvent permeability remains almost unaffected; the intermediate case is the solvent permeation throughout the isotropic (gas) phase. Herein, a permeability function $\kappa(\phi)$ in association with both the aspect ratio and the non-uniform orientation of the nanoplatelet is essentially desirable in the present study, which takes the following formula:4

$$\kappa(\phi) = \kappa_0 \frac{1 - \phi}{1 + \frac{\lambda}{3}\phi\left(s + \frac{1}{2}\right)},\tag{5}$$

where κ_0 indicates a reference value of permeability that we assume in the scaling law $\kappa_0 \sim a^2$ (akin to the hard sphere mode^{42,43}), and *s* is order parameter of the colloidal platelet varying between 0 (isotropic phase) and 1 (full nematic phase).

With the above set of equations, we can derive the volumeaveraged velocity of bulk nano-suspension as

$$\nu_{s} = \frac{\varepsilon^{2}}{12M(\phi) + \varepsilon^{2}Q(\phi)} \left(Q(\phi)\nu_{f} + D\lambda \frac{\partial \widetilde{\Pi}}{\partial x} \right), \tag{6}$$

where $\varepsilon = H/a$ acts as a geometric confinement parameter, $D = k_B T/2a\pi\eta_0$ is an average self-diffusion constant of an individual nanoplatelet, the dimensionless osmotic pressure is $\Pi = \Pi \sigma/k_B T$, and the symbol functions read as $M(\phi) = 1 + A_1\phi + A_2\phi^2$ and $Q(\phi) = \frac{1}{\phi} + \frac{\lambda}{3}(s + \frac{1}{2})$. The osmotic pressure which represents the

interplay between nanoplatelets at thermodynamic equilibrium is much more complicated than that for the spherical colloids owing to the signature of isotropic-to-nematic (I–N) phase transition. For a colloidal system given at a stable equilibrium, the osmotic pressure is functionally correlated with the free energy density.⁴⁶ Please see Methods in detail about the modeling of free energy density and osmotic pressure as used in this work.

To represent the applicable modeling of free energy density, it is important to predetermine the possible orientation of nanoplatelets arranged in the resulting nematic phase nearby the drying end. It is predictable that the colloidal platelet prefers to align with the flat surface parallel to its drifting direction as they are forced to drift toward the drying end in the reservoir because the friction ξ_{\parallel} is smaller than ξ_{\perp} for the aspect ratio $\lambda \gg 1$. However, once the nanoplatelet approaches the drying end, the exerted torque on the other edge of nanoplatelet by the solvent flow will turn it parallel to the drying edge (as a contact line), i.e., the flat surface of nanoplatelet becomes perpendicular to the solvent flow, which is supposed to achieve a maximum contact area between the nanoplatelet and the drying edge (treat it as a rigid wall). Due to a continuous migration of the nanoplatelets toward the drying edge, all nanoplatelets will be arrested with such an orientation as the concentration increases to form a nematic phase. On account of considerably fewer reports on the direct observations upon the arrangement of nanoplatelets when directional drying, the above analysis is supposed to be indirectly rationalized by the recent experiments and numerical simulations upon vertical drying of the suspensions containing colloidal rods.^{6,7,38,39} Strictly, whether the orientation configurations are variable in the resulting nematic phase, particularly when exposed to special external conditions such as evaporation rate, temperature, and even surface hydrophilicity/hydrophobicity, should be further examined. Whereas, we make sure that the scenario discussed above can most likely happen in an ordinary drying scenario. In this regard, for the sake of simplicity, we can assume that the oriented platelets in the nematic phase have the symmetry around the *x*-axis, and therefore $\phi_z = \phi_y$. The order parameter is then defined by

$$s = \frac{\phi_x - \phi_z}{\phi}.$$
 (7)

We can easily express the nanoplatelet concentrations in three species $\phi_{x,y,z}$ as the functions of total concentration ϕ and the order parameter *s*,

$$\phi_x = \frac{\phi}{3}(1+2s), \quad \phi_z = \phi_y = \frac{\phi}{3}(1-s).$$
 (8)

With this discrete order parameter mode (Zwanzig model³⁵), we can express the osmotic pressure (or in dimensionless form) as a complicated function of the concentration ϕ and the order parameter *s* (Methods shows more details).

By combining above set of equations, we can finally determine the equation of transport dynamics in the directional drying of colloidal platelet suspension in a confined H–S channel,

$$\dot{\phi} = v_f \frac{\partial \phi}{\partial x} + \varepsilon^2 \frac{\partial}{\partial x} \left(\frac{Q(\phi)v_f + D\lambda \frac{\partial \widetilde{\Pi}}{\partial x}}{12M(\phi) + \varepsilon^2 Q(\phi)} \right).$$
(9)

The corresponding boundary conditions are that (i) the nanoplatelet velocity v_p at the drying end is zero, and (ii) the mass flux of nanoplatelet at liquid–air interface in the reservoir is also zero, yielding

$$\left. v_s \right|_{x=0} = (1-\phi)v_f, \quad \left. \frac{\partial \phi}{\partial x} \right|_{x=L(t)} = 0.$$
 (10)

The above dynamic equation can be rewritten into its dimensionless form by introducing the applicable dimensionless variables,

$$\widetilde{x} = \frac{x}{L_0(1-\tau)}, \quad \tau = \frac{t\nu_f}{L_0}, \quad \widetilde{\nu}_s = \frac{\nu_s}{\nu_f}.$$
 (11)

Substituting Eq. (11) into Eqs. (6) and (9), we obtain the corresponding dimensionless equations, respectively,

$$\widetilde{\nu}_{s} = \frac{\varepsilon^{2}}{12M + \varepsilon^{2}Q} \left(Q + \frac{\lambda}{Pe(1-\tau)} \frac{\partial \widetilde{\Pi}}{\partial \widetilde{x}} \right), \quad (12)$$

$$\frac{\partial \phi}{\partial \tau} = \frac{1 - \widetilde{x}}{1 - \tau} \frac{\partial \phi}{\partial \widetilde{x}} + \frac{\varepsilon^2}{1 - \tau} \frac{\partial}{\partial \widetilde{x}} \left(\frac{Q + \frac{\lambda}{Pe(1 - \tau)} \frac{\partial \widetilde{\Pi}}{\partial \widetilde{x}}}{12M + \varepsilon^2 Q} \right), \quad (13)$$

where the drying Peclet number is defined by $Pe = L_0 v_f / D$. Apparently, the original moving boundary condition is now transferred into the fixed boundary condition as

$$\widetilde{\nu}_s|_{\widetilde{x}=0} = 1 - \phi, \quad \frac{\partial \phi}{\partial \widetilde{x}}\Big|_{\widetilde{x}} = 1 = 0.$$
 (14)

Equations (13) and (14) are the governing evolution equation and the boundary conditions to quantitatively determine the growth dynamics of nanoplatelet liquid crystals driven by the directional drying as confined in the H–S channel.

III. RESULTS AND DISCUSSIONA. I–N phase transition of nanoplatelet at thermodynamics equilibrium

We first present the I–N phase transition diagram of the colloidal platelet for various aspect ratio at thermodynamic equilibrium state in Fig. 2. As we reported in previous work,³⁶ the variation of order parameter with time is mainly proportional to the time ratio t_T/t_R with t_T and t_R being the characteristic time scales of translational motion and rotational motion, respectively. Within a simple slow flow, taking the thin-like alpha zirconium phosphate (α -ZrP) nanoplatelet for example, such a time ratio $t_T/t_R \gg 1$. Recalling the characteristic timescale is inversely proportional to the diffusivity, it is suggested that the rotational diffusivity is fairly larger than the translational diffusivity, as shown in Fig. 1(b). All these analyses indicate that the order parameter can relax to its equilibrium state very quickly as the nanoplatelets migrate in the flow of bulk suspension,^{36–39}

$$\frac{\partial f(\phi, s)}{\partial s} = 0. \tag{15}$$

Such a minimization of the free energy density with respect to the order parameter can determine the I–N transition phase diagram in Fig. 2. As seen in Fig. 2, there exists a transition concentration threshold, below which the order parameter remains zero meaning an isotropic phase, while above which the order parameter immediately changes to a certain non-zero value meaning a resulting nematic phase (or I–N coexisting phase). Such a concentration threshold ϕ_{I-N} triggering the I–N phase transition is apparently dependent on the nanoplatelet aspect ratio, namely, ϕ_{I-N} decreases with an increasing λ , indicating that the nematic phase can readily form with a smaller transition concentration in the thinner nanoplatelets. The results in the phase diagram reported here are not only consistent with Onsager's phase transition theory for the anisometric particles³² but also the experimental measurements by Cheng's group⁴⁰ as presented in Table I.

B. Effects of drying rate and aspect ratio

The drying system without confinement effect, i.e., the confinement parameter is set to $\varepsilon = 100$, is first addressed. We calculated the time evolution profiles of concentration and the order parameter of the nanoplatelets with $\lambda = 100$ for different drying rates, and show the results in Fig. 3. As the directional drying proceeds, water in the reservoir is evaporated continuously causing the viscous flow of the bulk suspension in the channel, and then the nanoplatelets experience a directional migration, as well as the liquid-air interface, toward the drying end. The concentration nearby the drying end increases gradually, while it still holds an initial value in the reservoir. The concentration increases substantially in the overall suspension, forming a dense particulate film in the channel as the water is going to be completely dried. Obviously, the faster the drying rate is, the more concentration increases at the drying end. In this work, we postulate a normal drying rate v_{f0} with the Peclet number $Pe_0 = 20$, and either below or above which the case will be regarded as a slow or fast drying, respectively.

As formerly mentioned, once the increasing concentration at the drying end exceeds the transition threshold ϕ_{I-N} , the nanoplatelets are orientationally aligned to form the nematic phase, which signifies that the order parameter changes from zero to a non-zero value immediately, as seen in Fig. 3. More importantly, from Fig. 3, we can identify three different domains with a large concentration gradient, i.e., the nematic phase domain, followed by the LST domain, and the reservoir domain in the H–S channel. These resulting domains specify two domain fronts, i.e., the nematic phase front L_{nem} and the LST front L_{tr} . These observations are comparable to the domain formations existing in the drying system of spherical colloids, i.e., the dense packing deposit, followed by the LST zone, and the reservoir zone, as reported in our previous study.¹³

Here, since the nematic phase forms at the drying end, the N phase front can be easily specified by focusing on the location the order parameter abruptly transforms from zero, which also can be

TABLE I. Comparisons in I–N phase transition of the colloidal platelets used in between the experiments⁴⁰ and this work.

Nanoplatelet model	Aspect ratio	I–N coexisting phase	Full nematic phase
ZrP in experiments Platelet in this work	$\lambda pprox 98 \ \lambda = 100$	$\phi_{I-N} {=} \ 0.040 \pm 0.002 \ \phi_{I-N} {=} \ 0.0382$	$\phi_N = 0.068 \pm 0.002 \ \phi_N = 0.072$



FIG. 3. Time evolution of the concentration (left column) and the order parameter (right column) for different drying rates: (a) for Pe=20; (b) for Pe=20; (c) for Pe=80. The inset in (b) presents the velocities of nanoplatelet (solid lines) and bulk suspension (dashed lines) over time, and the points represent the LST front where these two velocities diverge, i.e., the LST front receding in the channel. The parameters are $\lambda = 100$, $\varepsilon = 100$.

experimentally observed by crossed polarized optical images.^{34,40,47} The domain between the N phase domain and the reservoir domain is treated as the liquid–solid transition domain, but it is hard to determine the LST front L_{tr} visually. We can address the resulting LST front theoretically by examining the velocity profiles of the nanoplatelet and the suspension, as plotted in the inset in Fig. 3(b). It is seen that the nanoplatelets travel initially with the suspension at the same velocity v_f ($\tilde{v}_s = 1$) in the reservoir, while their velocities are divergent (\tilde{v}_s becomes smaller than 1) at a certain place as drying proceeds. After that, the nanoplatelets at the drying end. The divergence in their velocities indicates that the nanoplatelets start to pack more closely hindering their transport, which gives rise to a noticeable increase in concentration from ϕ_0 . In other words, the location at which the velocities \tilde{v}_s and \tilde{v}_p start to diverge is indicative of the formation of

intermediately concentrated domain, which behaves as a nature of LST domain. Then such a velocity divergence location can naturally serve as the LST front L_{tr} . We stress these locations by the solid points in the velocity profiles in the inset of Fig. 3(b), which clearly shows a dynamically receding LST front L_{tr} in the channel. As a matter of fact, the N phase front L_{nem} and the LST front L_{tr} move backward in the channel together but at different velocities. Accordingly, there should exist a transition layer between these two fronts captured by $\Delta L_{tr} = L_{tr} - L_{nem}$, and the phenomenon of such a transition layer is ubiquitous in the drying of the droplets and films.^{2–4,11}

The time evolutions of the transition layer and the N phase front, both are scaled by L_0 , are illustrated for different drying rates in Figs. 4(a) and 4(b), respectively. The drying rate, i.e., the drying Peclet number, is seen to impact on $\Delta L_{tr}(\tau)$ and $L_{nem}(\tau)$ greatly. During the early drying stage, the transition layer increases linearly with time in

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FIG. 4. Dynamics of (a) the transition layer ΔL_r and (b) the N phase front L_{nem} for varied drying rate, i.e., the drying Peclet number. Inset in (b) shows the different functional correlations of the instantaneous growth velocity of nanoplatelet nematic phase to time depending on the drying rate. The solid gray line in (b) presents the trajectory of liquid-air interface over time.

a double-log plot format, suggesting a power law-dependent variation $\Delta L_{tr}(\tau) \sim \tau^k$, for all Peclet numbers. The power index decreases ranging from 0.466 ± 0.003 to 0.185 ± 0.002 as *Pe* increases from 2 to 100. As the drying continues, however, the evolution behavior of the transition layer is appreciably dependent on drying rate Pe. For the slow drying rate, i.e., the small $Pe \leq 20$, the LST layer reduces very fast during the later drying stage, indicating that (i) the N phase front has formed and receded inwards the channel at an increasing rate, and (ii) the LST front has receded to combine with the liquidair interface, and subsequently, the LST front becomes the liquid-air interface to move toward the drying end, namely, the fronts L_{nem} and L_{tr} move in opposite directions making $\Delta L_{tr}(\tau)$ reduce rapidly. For the fast drying, i.e., Pe > 20, the layer $\Delta L_{tr}(\tau)$ could keep an increasing growth instead of reducing rapidly. Since the higher evaporation rate can often result in the faster backward LST front toward the liquid-air interface, we then argue that the length of LST layer increases gradually because the formed N phase domain becomes shortened for the faster drying. The profiles of front L_{nem} overtime for different drying rate as shown in Fig. 4(b) present the evidence for our argument. It is indicated that N phase front appears earlier as the drying rate increases, while the length of the front L_{nem} moving backward in the channel becomes shortened. For instance, when $Pe \leq 20$, the front L_{nem} can recede until it combines with the moving liquid-air interface, so that the N phase front becomes the liquid-air interface to move toward drying end (length of the nematic phase decreases) during the later drying stage, suggesting that the length of N phase is long as the total drying film; when Pe > 20, the length traveled by L_{nem} becomes shortened compared to that for small Peclet number during the total drying, and it even would not reach the liquid-air interface at the later drying stage [the front L_{nem} has the final location below the liquid–air interface trajectory as guided by the gray line in Fig. 4(b)]. These results can be understood as follows: the higher drying rate can significantly enhance the directional accumulation of colloidal platelets toward the drying end, which in turn creates the thinner dense packing layer.

That is to say, the resulting nematic phase domain could be naturally compressed as a bulk toward the drying end under a high drying rate.

One can also see that the N phase front evolves over time nonlinearly for all Peclet numbers, which is bound to suggest a timedependent instantaneous velocity of growing nematic phase. This behavior is more complicated than the time evolution of dense deposit front in drying the suspensions of spherical colloids.^{13,30,31} The instantaneous velocity of N phase front L_{nem} can be produced from the data as shown in Fig. 4(b) according to the definition $\frac{v_{nem}}{v_{\ell_0}} = \frac{Pe}{Pe_0} \frac{d}{d\tau} \left(\frac{L_{nem}}{L_0} \right)$, noticing that such a velocity has been scaled by the normal drying rate v_{f0} and Pe_0 for all range of drying rates *Pe*. Obviously, the growth velocity of nematic phase markedly increases with drying rate throughout the drying age. Moreover, it is found that the nematic phase velocity increases monotonically with drying time for the slow dryings $Pe \leq 20$, however, interestingly, v_{nem} displays a nonmonotonic variation with time, i.e., a decrease at first, followed by an increase, for the fast dryings Pe > 20. We also observe the phenomenon that the growth velocity of N phase rapidly increases, meanwhile the transition layer dramatically reduces, during the later drying stage. It can be well understood since all moving interfaces (or the fronts) are always seen to combine together very fast in the channel when the water will be completely dried, and this phenomenon has been referred to as the "rush hour" at the last moment of the drying of a droplet or a film.^{5,13} The nonmonotonic variation of the instantaneous velocity v_{nem} overtime for the fast dryings can be presumably explained as follows. The higher drying rate can not only allow the nematic phase to form more quickly with a larger velocity v_{nem} at initial time, but also force the nanoplatelets to orientationally align much denser in the packing deposit domain. In consequence, the concentration of nanoplatelet in the N phase greatly raises, while the growth rate of N phase slows down owing to the compacted packing of nanoplatelets, displaying a decreasing v_{nem} during intermediate drying time.

As the instantaneous velocity v_{nem} is a time-dependent variable, despite characterizing the dynamic behavior of growing nematic phase, we prefer another derivative variable, a time-averaged growth velocity of N phase $\langle v_{nem} \rangle$, in our following discussions. In this work, the later drying stage at time $\tau = 0.7$ is assumed to be a (quasi) equilibrium state at which the total length of dried film is $L_{equ} = 0.3L_0$. In this regard, the average velocity of growing N phase can be well defined with a dimensionless expression $\frac{\langle v_{nem} \rangle}{p_0} = \frac{Pe}{P_0} \frac{L_{om}^{0}}{L_{od} \lambda^2}$, where $L_{nem}^{0.7}$ is taken as an equilibrium length of resulting N phase at drying time $\tau^{0.7} = 0.7$, and $\Delta \tau = \tau^{0.7} - \tau^0$ is the so-called total growing time of N phase. Noticing that, as shown earlier, the starting time τ^0 to form the N phase is susceptible to the drying rate *Pe*. Herein, such a time-averaged velocity $\langle v_{nem} \rangle$ helps us access conveniently how the macroscopic drying behaviors of nanoplatelet suspensions are correlated with the drying rate, aspect ratio, and also geometric confinement.

The aspect ratio $\lambda = a/b$ is an important feature of the colloidal platelets differing from the colloidal spheres. We would like to probe the resultant of the aspect ratio and the drying rate on the growth behavior of the resulting nematic phase at the equilibrium drying. Figures 5(a) and 5(c) display the equilibrium length $L_{nem}^{0.7}$ of resulting N phase, and its average growth velocity $\langle v_{nem} \rangle$ for a broad range of parameter plane of *Pe* and λ , respectively. As one can see in Fig. 5(a), the equilibrium length of the N phase formed by the thicker nanoplatelets is apparently shorter than that of the N phase formed by the thinner nanoplatelets, i.e., $L_{nem}^{0.7}$ declines as λ reduces from 100 (thin platelet) to 30 (thick platelet), for all range of drying rates. In reality, the thicker nanoplatelets require the higher I-N transition concentration to form nematic phase, as shown in Fig. 2. That is to say, the N phase front for thick nanoplatelet should be much closer to the drying end than that for thin platelet during overall drying, which eventually leads to the shorter equilibrium length of N phase.

Although the aspect ratio can significantly alter the equilibrium length of N phase, The correlations between the length $L_{nem}^{0.7}$ and the drying rate is consistent for all nanoplatelet types, illustrating a monotonic decrease in $L_{nem}^{0.7}$ with an increasing drying rate. It is indicated

that the nematic phase is compressible when subjected to the enhanced drying rate. However, some differences in $L_{nem}^{0.7}$ varying with Pe still exist for the varied aspect ratios as shown in Fig. 5(a). For the thin-like nanoplatelets, $\lambda \geq 70$, the equilibrium N phase length takes a constant about $L_{nem}^{0.7} = 0.3$ in a very slow drying range Pe < 10, indicating a combination between the N phase front and the liquid-air interface. Then, the N phase has the same length as the total dried film at $\tau = 0.7$ before being compressed by the enhanced drying rate. In contrast, for the thick-like nanoplatelets $\lambda < 70$, the N phase front $L_{nem}^{0.7} < 0.3$ is hard to reach the liquid–air interface in the slow drying range such that the compressive effect by the enhanced drying rate on the growing N phase prevails. One then observes a direct decrease in the equilibrium N phase length with the increasing drying rate. Besides, compression rate of the N phase formed by the thin-like nanoplatelets with regard to the increasing Pe is uniform [the slopes in Fig. 5(a)], while it is not the case for the thick-like nanoplatelets, for example, the nanoplatelet with $\lambda = 30$, the compression rate in the slow drying range $Pe \leq 20$ is larger than that in the fast-drying range Pe > 20.

In order to produce the average growth velocity of N phase, we exhibit the total growing time $\Delta \tau$ in correlation to drying rate for different aspect ratios in Fig. 5(b). As expected, the higher drying rate is, the longer time N phase takes to grow, because the starting time τ^0 to form the N phase is shortened as the drying rate enhances. In addition, as shown in Fig. 5(b), the growing time of N phase for the thick nanoplatelets is much shorter than that for the thin ones, particularly in the slow drying range. To understand this observation, we argue that triggering the I–N phase transition for the thicker nanoplatelets requires a higher transition concentration ϕ_{I-N} . Therefore, the formation of N phase forms, throughout the drying process, particularly under the slow drying. In other words, the time the N phase of thicker nanoplatelets takes to



FIG. 5. The resultant of drying rate and aspect ratio on (a) the equilibrium length, (b) the total growing time, and (c) the time-averaged growth velocity of nanoplatelet liquid crystals.

grow is evidently shortened, in particular in the slow drying range *Pe* \leq 20. Herein, the average growth velocity $\langle v_{nem} \rangle$ of N phase can be numerically produced by the data from Figs. 5(a) and 5(b) according to its definition mentioned above, and is displayed in Fig. 5(c). It is seen that the velocity $\langle v_{nem} \rangle$ monotonically increases with drying rate as a bulk for all nanoplatelet types, while the variance in $\langle v_{nem} \rangle$ caused by the aspect ratio also depends on the drying rate. In the fast-drying range, the average velocity $\langle v_{nem} \rangle$ almost converges together independently from aspect ratio, which can be well fitted by a linear function of Pe in log-log format, i.e., suggesting a power law function between them $\langle v_{nem} \rangle \sim Pe^k$ with a power index $k = 0.636 \pm 0.002$. Such a velocity varying with Pe, however, is noticeably altered by the aspect ratio in the slow drying range, showing that the nematic phase of thicker nanoplatelets achieves the larger average growth velocity $\langle v_{nem} \rangle$. The linear correlation of $\langle v_{nem} \rangle$ to *Pe* can still remain in the slow drying range, but appears in different slopes depending on the aspect ratio as seen in Fig. 5(c).

These results demonstrate that the drying behaviors of the colloidal suspensions in a fast-drying regime can be highly uniform, which is affected little by the nanoparticle types, like shape and size. Whereas, these drying behaviors appear divergently in a slow drying regime because the arrangement of the nanoparticles with either spherical or non-spherical shape is reorganizable in time in the resulting liquid crystalline phase. The drying rate plays a vital role in regulating the growth dynamics of these structural phases.

C. Growing liquid crystals under confinement

We now focus on discussions about the effects of geometric confinement exerted by the H–S channel wall on the drying behaviors of colloidal platelet suspensions. The following calculations were performed for the thin-like nanoplatelet $\lambda = 100$. Notice that the enhanced confinement may also result in the excluded volume effect of particles near the confined walls.¹³ In other words, as the wall gap reduces, since the center of the particle is unable to penetrate the walls, an effective height for the confined particles becomes H - 2a, and then this gives rise to an effective volume fraction higher than that in the bulk by $\phi_{eff} = \phi/(1 - 2/\varepsilon)$ with the square cross-section geometry in the H–S cell. The fraction of excluded volume becomes more important as the wall gap decreases.

We show evolution profiles of N phase front for different confinement parameters $\varepsilon = H/a$ under a normal drying rate Pe = 20 in Fig. 6, i.e., the growing nanoplatelet liquid crystals under the confinement. It is found that the enhanced confinement (a decreasing ε) can not only allow the N phase to form earlier at the drying end, but also achieve the longer N phase domain throughout the drying process. As seen in Fig. 6, the growth of N phase could be assigned to three local stages, namely, beginning, intermediate, and final stages, with the approximately linear correlations to time, though the overall profile of N phase varies nonlinearly with time. Herein, the instantaneous velocity (scaled by v_{f0}) of growing N phase can be approximately given by the slope of linear profiles in these local stages. Apparently, the growth velocity of N phase is noticeably enhanced by the confinement from the channel, in particular from the beginning to the intermediate drying stages. These results suggest that the confinements can result in an enhanced directional drying process in which the accumulation of nanoplatelets toward the drying end is promoted, which closely resembles the effect arising from an increasing drying rate in the model. The



FIG. 6. Time evolution of nanoplatelet nematic phase front under different geometric confinements. The parameters are Pe=20, $\lambda=100$.

present measurements for nanoplatelets are in accordance with our previous results¹³ and the experimental observations³¹ for the colloidal spheres. Moreover, these drying behaviors observed here remain almost unaffected as the confinement is weakened toward about $\varepsilon \geq 40$.

Clarifying the collaboration of the confinement parameter ε and the drying Peclet number Pe on a directional drying in a confined channel is of particular interest in many experimental studies and engineering practices. To this end, we explore how such a resultant of parameters ε and Pe impacts on growth of the nanoplatelet liquid crystals. Recalling the profiles in Fig. 5(a), the receding N phase front for the thin-like nanoplatelet has combined with the liquid-air interface at time $\tau = 0.7$, i.e., the equilibrium length $L_{nem}^{0.7} = 0.3$, within the range of small Pe. To avoid this situation in which the N phase front changes into the liquid-air interface moving forwards to the drying end, we stopped the calculations at time $\tau = 0.6$, and adopted $L_{nem}^{0.6}$ as the final length of N phase, as well as $\langle v_{nem}^{0.6} \rangle$ as the corresponding timeaveraged growth velocity of N phase, for all range of drying rates Pe. We plot the final length of N phase and its average growth velocity as the functions of the confinement parameter for different drying Peclet numbers in Figs. 7(a) and 7(b), and both of which are plotted as the functions of Peclet number for different confinement parameters in Figs. 7(c) and 7(d), respectively.

We find that the final length $L_{nem}^{0.6}$ and the velocity $\langle v_{nem}^{0.6} \rangle$ both appreciably increase with the enhanced confinement (a decreasing ε), as shown in Figs. 7(a) and 7(b), for all range of *Pe*. This manifests the role the geometric confinement plays in facilitating the growth of nanoplatelet liquid crystals, agreeing with the results we discussed above in Fig. 6. In addition, as seen in Figs. 7(c) and 7(d), the final length of N phase shortens, while its average growth velocity improves, with the enhanced drying rate. But, their linear correlations to the drying Peclet number still maintain in log-log format for the variable



FIG. 7. (a) The final length of nanoplatelet liquid crystals and (b) its average growth velocity are plotted against the confinement parameter with the varied drying Peclet numbers. The same data of (a) and (b) plotted against the drying Peclet number with the varied confinement parameters in (c) and (d), respectively.

confinements, showing a similar trend compared to Fig. 5. Furthermore, Figs. 7(a) and 7(b) also show that either the final length or the average growth velocity remains almost unaffected as long as the confinement parameter increases above a threshold value which highly depends on the drying rate.

Collecting the paired data comprising the Peclet number and the corresponding confinement threshold, we can produce a boundary curve based on these points, which allows us to access the condition regimes in which whether the geometric confinement prevails or not. Under this consideration, Fig. 8 illustrates the state diagram in the plane $\varepsilon - Pe$ for the drying system of the colloidal platelets, and also for the drying systems of the (charged) colloidal spheres which exist for the comparisons together. It suggests that all the points collected from the profiles of the length $L_{nem}^{0.6}$ and the average velocity $\langle v_{nem}^{0.6} \rangle$ in Figs. 7(a) and 7(b) almost fall onto one master curve which is well represented by the linear fitting. For the comparisons, we also present the data used to provide the boundary curves for the cases of colloidal spheres (please see data collections in Methods) in the same state diagram for the nanoplatelets. Interestingly, the master curve that is produced by either the theoretical¹³ or the experimental measurements³¹ for the colloidal spheres still appears linearly, but with a larger slope than that for the nanoplatelets. Apparently, for each case, the boundary line denotes the criterion that the drying system in the condition regime below the line (the colored areas in Fig. 8) is significantly susceptible to the geometric confinement, or otherwise, the confinement effect could be negligible in the condition regime above the line. The state diagram presented here unmasks a scenario that it is universal for the drying rate to be linearly correlated with the geometric confinement in the unidirectional drying systems, with the insignificant effects arising from the nanoparticle shape and surface charge, and furthermore, it also predicts that the enhanced confinement exerted by the channel can directly lead to the increase in evaporating flux of water because all the slopes of boundary lines are negative, which is in accord with both previous theoretical and experimental observations.¹³ Since the slope (absolute value) of the boundary line for the nanoplatelets is smaller than that for the colloidal spheres, as shown in Fig. 8, which helps to access a signature that the enhancement in evaporating flux of water in drying the colloidal platelet suspension is supposed to be much weaker than that in drying the colloidal sphere suspension, when exposed to the enhanced geometric confinement. As the lateral size of nanoplatelet is comparable to the diameter of nanosphere, namely, the difference in their average collective diffusivity is insignificant, the occurrence of this signature, we speculate, is most likely because that the nanoplatelet nematic phase is formed at the drying end with the structural configuration of compacted layered arrangement, which consequently achieves the stronger water retention compared to that in the packing deposit of colloidal spheres formed with the percolated morphology. It is hoped that all these numerical findings conducted by our theoretical framework can be well tested by the pertinent drying experiments for the platelet-like materials in the near future.

As is well known, the nanoplatelets can display much richer phase configurations than the spherical nanoparticles as the concentration exceeds the transition threshold value, in this regard, whether the resulting nanoplatelet liquid crystals can form with the more complicated phase configurations, for instance, columnar (C) phase, and smectic (S) phase, at the drying end by regulating the unidirectional drying conditions, and how these formed diverse phase configurations can, in turn, affect the drying behaviors of nanoplatelet suspensions should be well addressed by future numerical and experimental research. Although the direct supporting experiments still await, the validity of our simple theory can be guaranteed with elaborate



FIG. 8. State diagram in the parameter plane of ε – *Pe* illustrating the condition domains where the confinement effect dominates, i.e., the colored areas below the boundary lines, for each case of the thin-like nanoplatelets (λ = 100, left panel), the charged spherical colloids (radius *a*= 100 nm, medium panel),¹³ and the colloidal silica spheres (mean diameter *d* = 110 nm, right panel).³¹ The preparation of data collected from Refs. 13 and 31 is presented in the Appendix.

modeling derivations and calculations, which can be confirmed by referring to the indirect experiments by Shinde *et al.*⁴⁰ and the comparisons with recent simulations and experiments for drying of spherical colloids suspensions.^{13,31} The theoretical framework we have developed here can serve as a significant step forward to deeply understanding the growth dynamics of liquid crystals of colloidal platelet-like materials driven by unidirectional solvent evaporation under a confinement environment, and can also be readily generalized to deal with those aforementioned studies. It is our expectation that our findings require careful explorations by future experimental and numerical research.

IV. SUMMARY

We have demonstrated the directional drying-induced growth dynamics of nanoplatelet liquid crystals in the confined H–S channel by developing the theoretical framework. Our numerical measurements show that the growth dynamics of nanoplatelet liquid crystals is highly susceptible to drying rate (Peclet number), aspect ratio of nanoplatelet, and geometric confinement of H–S channel.

The instantaneous velocity of growing N phase is timedependent because the motion of N phase front is found to vary nonlinearly with drying time. Such a velocity increases monotonically with time for the slow dryings, while varies nonmonotonically with time for the fast dryings, i.e., reducing initially followed by increasing. All these observations strikingly differ from the drying system of spherical colloids.^{13,28–31} We demonstrate that the enhanced drying rate can significantly compress the N phase toward the drying end, but improve its time-averaged growth velocity for all nanoplatelet types. It therefore comes to an argument that the fast-drying regime enables the growth behaviors of N phase more uniform, but by contrast, these behaviors appear in variance in the slow drying regime depending on the nanoplatelet types, for example, the nematic phase formed by the thicker nanoplatelet achieves the higher average growth velocity, but gets the shorter final length in the channel.

Moreover, the geometric confinement is shown to enhance the growth of nanoplatelet liquid crystals markedly. A state diagram was produced to further clarify the linear functional dependence of drying Peclet number to confinement parameter threshold, serving as the boundary line in specifying the condition regimes where whether the confinement effects prevail or not, for both platelet and sphere systems. Since all these boundary lines appear with negative slopes, we then identify that the enhanced confinement allows the strengthened drying flux of solvent, and such behavior appears as a universal signature in the unidirectional drying protocol. However, the enhanced drying flux for the nanoplatelet system is several orders of magnitude lower than that for the spherical colloids system, which is indicative of favorable water retention in the compacted nematic architecture prevailing over the porous percolation deposits formed by the spherical colloids. Our present theoretical framework could exhibit remarkable extensibility to explore self-assembly dynamics of the nanomaterials with other shape anisotropy and other out-of-equilibrium pathways, such as filtration and thermophoresis-driven protocols.

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

APPENDIX A: FREE ENERGY DENSITY AND OSMOTIC PRESSURE

In this work, the nanoplatelet was modeled by thin discotic colloids with diameter 2*a* and thickness 2*b*, assuming $a \gg b$, as shown in Fig. 1(c). The nanoplatelet with this morphology has been

widely employed as the ideal candidate in exploring the rich phase behaviors arising from self-assembly induced by a variety of external approaches.^{1,40,47}

In the main text, our continuous model was derived on the basis of viscous flow of complex nanofluid confined to an H–S channel, involving the platelet orientation-dependent permeability in the modified Darcy's law for resulting crystalline phase and the interactions between nanoplatelets based on exclusion volume theory which is valid for a large range of concentration. Since we have assumed that the nanoplatelet is orientated discretely along x, y, and z axis, which is termed as Zwanzig mode, the free energy density (per unit volume) at the thermodynamic equilibrium can simply read as

$$f(\phi, s) = k_B T \left(\frac{2}{\sigma} \phi_z \ln \phi_z + \frac{1}{\sigma} \phi_x \ln \phi_x\right) + f_{exc}(\phi, s).$$
(A1)

In Eq. (A1), the first term on right side means a normal free energy density originating from entropy-driven contribution, and the second term is so-called excess free energy density which addresses the interactions between nanoplatelets, involving both excluded volume entropy and orientational entropy.

Such an excess free energy density which adapts to the Zwanzig mode of order has been suggested into a reduced expression by Harnau *et al.* for the thin platelet-like particle,³³ which we cite as follows:

$$f_{exc}(\phi, s) = k_B T \left(-\frac{\phi}{\sigma} \ln(1-\phi) + \frac{n_1 \cdot n_2}{1-\phi} + \frac{n_{2,x} n_{2,y} n_{2,z}}{(1-\phi)^2} \right), \quad (A2)$$

where n_1 and n_2 are the vectors with $n_{2,x}$, $n_{2,y}$, and $n_{2,z}$ being the components of n_2 along three coordinate axes. These two vectors are expressed as follows according to the present problem:

$$\boldsymbol{n}_{1} = \frac{1}{\sigma} \begin{pmatrix} b\phi_{z} + a\phi_{y} + a\phi_{x} \\ a\phi_{z} + b\phi_{y} + a\phi_{x} \\ a\phi_{z} + a\phi_{y} + b\phi_{x} \end{pmatrix},$$
(A3)

$$\boldsymbol{n}_{2} = \frac{a}{\sigma} \begin{pmatrix} a\phi_{z} + b\phi_{y} + b\phi_{x} \\ b\phi_{z} + a\phi_{y} + b\phi_{x} \\ b\phi_{z} + b\phi_{y} + a\phi_{x} \end{pmatrix}.$$
 (A4)

Combining Eqs. (7) and (8) in the main text and Eqs. (A1)–(A4), we therefore express the total free energy density $f(\phi, s)$ as the complicated function of concentration ϕ and order parameter *s*.

To determine the phase diagram for an I–N phase transition in plane of $s - \phi$, the equation of state Eq. (15) should be numerically solved. As shown in Fig. 2 and in Table I, the transition concentration ϕ_{I-N} for I–N coexisting phase and the concentration ϕ_N for full nematic phase predicted by the present free energy density modeling agrees with the experimental data well for the thin ZrP nanoplatelet,⁴⁰ which is indicative of the model's validity.

For a given colloidal system at the thermodynamic equilibrium,⁴⁶ the osmotic pressure is functionally correlated with the free energy density by $\Pi(\phi, s) = -f(\phi, s) + \phi \partial f(\phi, s) / \partial \phi$. The dimensionless format then reads $\widetilde{\Pi} = -\widetilde{f}(\phi, s) + \phi \partial \widetilde{f}(\phi, s) / \partial \phi$ with

 $f(\phi, s) = f(\phi, s)\sigma/k_BT$ being the dimensionless free energy density. Accordingly, with above set of equations, we give the dimensionless osmotic pressure by following expression:

$$\widetilde{\Pi}(\phi, s) = \frac{\phi}{27\pi^2\lambda(1-\phi)^3} \left(27\pi^2\lambda(1-\phi)^2 + 2\phi^2\left(2s^3(\lambda-1)^3 - 3s^2\lambda(\lambda-1)^2 + (\lambda+2)^3\right) + 9\pi\phi\left(2s^2(\lambda-1)^2(\phi-1) + \lambda(5+2\lambda-3\phi-2\lambda\phi)\right)\right).$$
(A5)

Such an expression in Eq. (A5) has been invoked in the governing Eq. (9) or (13) in the main text.

APPENDIX B: DATA COLLECTIONS FOR COMPARISONS

The data for the case of colloidal spheres appearing as the comparisons in-state diagram Fig. 8 were produced from the theoretical work¹³ and the experimental work,³¹ respectively. (i) The theoretical work is our previous study about the lateral drying of the suspension containing the charged spherical colloids in a confined H–S channel. In order to compare to the case of nanoplatelet, we have reperformed the calculations for the dried suspension of the spherical colloids with following conditions: the nanosphere radius *a* = 100 nm, surface charge density γ = 0.033 (e nm⁻²), and monovalent salt concentration in ambient solution n_0 = 1 mM, which are the normal conditions discussed in our previous theoretical framework.

Following a similar approach, we calculated the profiles of dense deposit front at the later drying time $\tau = 0.6$ in a broad range of $\varepsilon - Pe$ plane, and the boundary point, beyond which the deposit front remains unaffected by confinement parameter, was naturally determined for every drying rate Pe we considered. However, a small point to note is that we desire to consider the dense deposit front here as the position in the channel where the concentration of spherical colloids reaches $\phi_g = 0.5$, a value that was recently suggested by an experimental measurement in Noirjean *et al.*'s study for drying system of silica nanospheres.¹² Although it is slightly different from the randomly close packing concentration of spheres $\phi_c = 0.64$ which is frequently used as an ideal theoretical reference value, we still ensure the validity of the concentration $\phi_g = 0.58$ in specifying the dense deposit front for the spherical colloids.

(ii) The experimental work cited here was implemented by Abe and Inasawa, which addressed the enhancement of drying flux from a narrow cell with variable height during a directional drying of the suspension containing the spherical silica colloids.³¹

The silica nanosphere used in the experiments has the mean diameter d = 110 nm, and the height of drying cell varies by H = 50, 100, 200 μ m, which gives the variable confinement parameters by $\varepsilon = 2H/d = 909$, 1818, 3636, respectively. Revisiting the definition of drying Peclet number $Pe = Lv_f/D$, the three involved physical quantities should be confirmed. The average diffusion constant of silica nanosphere was given by $D \approx 4 \times 10^{-12}$ (m² s⁻¹) at 20 °C. The length *L* appears here as a characteristic length for the

growing particulate film in the drying cell, and as they estimated, a given $L = 4 \mu m$ leads to Pe= 1. Herein, to avoid an extra-large Peclet number, we address *L* as the time-averaged length of resulting particulate film in *Pe* for the varied *H*, which can be done easily based on the profiles in Fig. 5 from Ref. 31. Furthermore, the time-averaged drying flux of water J_{av} (g m⁻² s⁻¹) was measured to significantly enhance with a decreasing *H*, i.e., an enhanced confinement, and the water evaporation rate can be therefore simply determined by $v_f = J_{av} / \rho_f$ with water density $\rho_f = 1000$ (kg m⁻³) at 20 °C. The discrete values of J_{av} corresponding to the varied cell height *H* can be readily captured from Fig. 4 in their paper. Hereto, we can produce the paired data (ε , *Pe*) used for the comparisons in-state diagram Fig. 8 according to those experimental measurements mentioned above.

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