Supplemental Material

Dynamics of the floating nematic phase formation in platelet suspension with thickness polydispersity by sedimentation

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1. Free energy density for the binary mixture of thin and thick hard platelets

We consider a colloidal suspension (with the total height h) consisting of platelet-like particles in two species i=1, 2 with the thickness L_i (assuming L_1<L_2) and the identical lateral size D. The parameters are the volume of individual platelet $\sigma_i = L_i D^2$, aspect ratio $\lambda_i = D/L_i$ and thickness ratio $\varepsilon = L_1/L_2$, so $\lambda_2 = \varepsilon\lambda_1$.

Here, we adopt the generalized Zwanzig model for determining the normal directions of sedimenting platelets, whereby they can take only three orientations along the x, y, and z axes.

The total volume fraction of particles is written as $\phi_i = \phi_i^x + \phi_i^y + \phi_i^z$, and we assume that the nematic phase has symmetry around z axis and therefore $\phi_i^x = \phi_i^y$. Then the nematic order parameter is introduced by

$$s_i = \frac{\phi_i^z - \left(\phi_i^x + \phi_i^y\right)/2}{\phi_i} = \frac{\phi_i^z - \phi_i^x}{\phi_i} \qquad (S1)$$

Alternatively, $\phi_i^x, \phi_i^y, \phi_i^z$ can be written as functions of ϕ_i and s_i as

$$\phi_i^x = \phi_i^y = \frac{1}{3}\phi_i(1 - s_i),\ \phi_i^z = \frac{1}{3}\phi_i(1 + 2s_i) \qquad (S2)$$

In the present system, the normal free energy density is

$$f_{nom} = k_B T\left(2\sum_{i=1,2}\frac{\phi_i^x}{\sigma_i}\ln\phi_i^x + \sum_{i=1,2}\frac{\phi_i^z}{\sigma_i}\ln\phi_i^z\right) \qquad (S3)$$

Here, the excess free energy density is calculated by the model proposed by Hansen et al. [1],

$$f_{ex} = k_B T\left[-\left(\frac{\phi_1}{\sigma_1} + \frac{\phi_2}{\sigma_2}\right)\ln\left(1 - \phi_1 - \phi_2\right) + \frac{n_1 \cdot n_2}{1 - \phi_1 - \phi_2} + \frac{n_{2,x}\,n_{2,y}\,n_{2,z}}{\left(1 - \phi_1 - \phi_2\right)^2}\right] \qquad (S4)$$

where the $n_{2,\alpha}$ is the projection of vector n_2, and the vectors n_1 and n_2 are given as

$$n_1 = \sum_{i=1}^{2}\begin{pmatrix} L_i\phi_i^x + D\phi_i^y + D\phi_i^z \\ D\phi_i^x + L_i\phi_i^y + D\phi_i^z \\ D\phi_i^x + D\phi_i^y + L_i\phi_i^z \end{pmatrix}\frac{1}{\sigma_i} \qquad (S5)$$

$$n_2 = \sum_{i=1}^{2} \begin{pmatrix} D\phi_i^x + L_i\phi_i^y + L_i\phi_i^z \\ L_i\phi_i^x + D\phi_i^y + L_i\phi_i^z \\ L_i\phi_i^x + L_i\phi_i^y + D\phi_i^z \end{pmatrix} \frac{D}{\sigma_i} \qquad (S6)$$

In consequence, the total free energy density is expressed as

$$f(\phi_i, s_i) = f_{nom} + f_{ex} \qquad (S7)$$

In this Letter, we modify the above free energy model by only keeping the terms on the right hand side of Eq. (S4) within the second order terms.

Accordingly, the dimensionless free energy density is given by (the Eq. 2 in the main text)

$$\begin{aligned} \frac{\sigma_1}{k_B T} f(\phi_i, s_i) \\ &= \frac{1}{3}[3\phi_1 \ln \phi_1 + 3\varepsilon\phi_2 \ln \phi_2 + 2\phi_1(1 - s_1)ln(1 - s_1) + 2\varepsilon\phi_2(1 - s_2)ln(1 - s_2) + \phi_1 \\ &+ \frac{1}{3}\sum_{i,j} \alpha_{i,j}\phi_i\phi_j s_i s_j + \frac{1}{3(1 - \phi_1 - \phi_2)^2}\sum_{i,j} \beta_{i,j}\phi_i\phi_j \end{aligned}$$

(S8)

where the coefficients $\alpha_{i,j}$ and $\beta_{i,j}$ are given as

$$\alpha_{1,1} = 4 - \frac{2}{\lambda_1} - 2\lambda_1$$

$$\alpha_{2,1} = \alpha_{1,2} = \frac{1}{2}\left[4(1 + \varepsilon) - \frac{4}{\lambda_1} - 4\varepsilon\lambda_1\right]$$

$$\alpha_{2,2} = 4\varepsilon - \frac{2}{\lambda_1} - 2\varepsilon^2\lambda_1$$

(S9)

$$\beta_{1,1} = 5 + \frac{2}{\lambda_1} + 2\lambda_1$$

$$\beta_{1,2} = \beta_{2,1} = \frac{1}{2}\left[5(1 + \varepsilon) + \frac{4}{\lambda_1} + 4\varepsilon\lambda_1\right]$$

$$\beta_{2,2} = 5\varepsilon + \frac{2}{\lambda_1} + 2\varepsilon^2\lambda_1$$

(S10)

2. Onsager principle for theoretical derivations

Onsager principle has been applied in diverse soft matter dynamics [2,3]. Here, we derive the non-equilibrium equation systems by using the Onsager variational principle.

The principle states that the time-evolution equations are obtained by minimizing the Rayleighian defined by

$$R = \dot{A} + \Phi \qquad (S11)$$

where $\dot{A}$ is the time derivative of the total free energy and Φ is the dissipation function.

The total free energy in the binary mixture of colloidal platelets read as

$$A = \int_0^h dz \left[f(\phi_i, s_i) + \sum_{i=1,2} \phi_i \rho g z\right] \qquad (S12)$$

Then, By Eq. (S12), $\dot{A}$ is calculated as

$$\dot{A} = \int_0^h dz \left[\sum_{i=1,2} \frac{\partial f}{\partial \phi_i}\dot{\phi}_i + \sum_{i=1,2} \dot{\phi}_i \rho g z \right] \qquad (S13)$$

Note that ϕ_i satisfies the conservation law

$$\dot{\phi}_i = -\frac{\partial \phi_i v_i}{\partial z} \qquad (S14)$$

where v_i is the velocity of the two species of particles. Hence, $\dot{A}$ is written using the integral by parts as

$$\dot{A} = \int_0^h dz \left[\sum_{i=1,2} \phi_i v_i \frac{\partial}{\partial z}\left(\frac{\partial f}{\partial \phi_i}\right) + \rho g \sum_{i=1,2} \phi_i v_i \right] + \int_0^h dz \sum_{i=1,2} \frac{\partial f}{\partial s_i}\dot{s}_i - \sum_{i=1,2} \phi_i v_i \left(\frac{\partial f}{\partial \phi_i} + \rho g z \right)\Big|_{z=h}$$

(S15)

We assume that the energy dissipation function in this problem can be formulated in simple form as

$$\Phi = \frac{1}{2}\int_0^h dz \left(\sum_{i,j=1,2} \frac{\phi_i}{\sigma_i}\zeta_{i,j}^T v_i v_j + \sum_{i,j=1,2} \frac{\phi_i}{\sigma_i}\zeta_{i,j}^R \dot{s}_i \dot{s}_j \right) \qquad (S16)$$

where $\zeta_{i,j}^T$ and $\zeta_{i,j}^R$ are translational friction coefficients and rotational friction coefficients per volume particles. In the dilute suspension, the hydrodynamic interactions can usually be ignored to assume that $\zeta_{1,2}^T = \zeta_{2,1}^T = 0$, and $\zeta_{1,2}^R = \zeta_{2,1}^R = 0$, and then the translational friction coefficients are expressed by using the Einstein relations as $\zeta_{1,1}^T = \zeta_{2,2}^T = k_B T / D_T$ and $\zeta_{1,1}^R = \zeta_{2,2}^R = k_B T / D_R$, where D_T and D_R are the translational diffusion coefficient and the rotational diffusion coefficient. Both of two coefficients are insensitive towards the thickness of particles since they are scaled by $D_T \sim k_B T / \eta D$ and $D_R \sim k_B T / \eta D^3$ with η the solvent viscosity. Generally, these coefficients vary with concentration due to the hydrodynamic interactions, but here we assume them as the constants for simplicity.

The translational velocity of the sedimenting platelets v_i is obtained by the minimizing condition $\partial R / \partial v_i = 0$, which gives

$$\sum_{j=1,2} \frac{\phi_i}{\sigma_i}\zeta_{i,j} v_j = -\phi_i \left(\frac{\partial}{\partial z}\left(\frac{\partial f}{\partial \phi_i}\right) + \rho g \right) \qquad (S17)$$

Similarly, $\dot{s}_i$ is obtained by $\partial R / \partial \dot{s}_i = 0$. By combining with Eqs. (S14) and (S17), the time-evolution equations are given as

$$\frac{\partial \phi_i}{\partial t} = \frac{\partial}{\partial z}\left[\frac{D_T \sigma_i}{k_B T}\phi_i \left(\frac{\partial}{\partial z}\left(\frac{\partial f}{\partial \phi_i}\right) + \rho g \right) \right] \qquad (S18)$$

$$\frac{\partial s_i}{\partial t} = -\frac{D_R \, \sigma_i \, \partial f}{\phi_i k_B T \partial s_i} \qquad (S19)$$

The boundary conditions are that the particle velocity v_i is zero at the bottom and the top of the suspension.

$$v_i(0,t) = v_i(h,t) = 0 \qquad (S20)$$

We assume that the binary mixture is initially homogeneous and isotropic, i.e., $s_i(z,0) = 0$, and $\phi_i(z,0) = \phi_{0i}$.

Furthermore, we can also simply the non-equilibrium equation of nematic order parameter Eq. (19). When the colloidal platelets sediment in a solution, they undergo both the translation motion and rotational motion. Commonly, the characteristic time t_R of rotation for causing s_i is less than that of translation t_T for ϕ_i in several magnitude. Since $t_R \sim \eta D^3/k_BT$, and $t_T = l_g/v_T$ with $l_g = k_BT/mg$ the sedimenting length of the particles and $v_T = D_Tmg/k_BT$ the characteristic sedimenting velocity of the particles, then the time ratio t_T/t_R is proportional to $(l_g/D)^2$. We evaluate this ratio by considering the data in Lekkerkerker et al.'s experiment for the gibbsite platelets [4], the diameter is $D \cong 170$ nm, the thickness is $L \cong 20$ nm, and the buoyant density $\rho^* \cong 0.7$ g/cm^3 (density of the grafted gibbsite is 1.7 g/cm^3), then the sedimentation length is calculated as $l_{g1} \cong 1$ mm, as a result $t_{T1}/t_{R1} \cong 3.57\times10^7$. Herein, it is usually a very large value.

The above discussion gives the conclusion that the s_i can reach its equilibrium value rapidly, namely Eq. (S19) can be reduced to the simple equilibrium equation as

$$\frac{\partial f}{\partial s_1} = \frac{\partial f}{\partial s_2} = 0 \qquad (S21)$$

which is the equation (4) in the main text.

As discussed above, the Peclet number for the thin platelets may have a normal value as $Pe_1 = h/l_{g1} = 20$ by considering the regular sample height $h = 2$ cm (a standard height of the container often used in the labs).

3. Phase diagram for I-N phase transition of bi-disperse platelets

3.1 Calculation for the nematic order s_2 as a function of s_1

In the main text, the Eq. 4 indicates essentially three equations, i.e., $\frac{\partial f}{\partial s_1} = 0$, $\frac{\partial f}{\partial s_2} = 0$, and $\frac{\partial f}{\partial s_2} = \frac{\partial f}{\partial s_1}$. By solving the first two equations, one can obtain the solutions written by $\phi_1(\phi_2, s_1, s_2)$, and $\phi_2(\phi_1, s_1, s_2)$, respectively. Interestingly, the relationship between s_1 and s_2 can be derived if one solve the last equation analytically, which can be expressed as Eq. (S22) or Eq. (5) in main text. Once again, substituting Eq. (S22) into the solution $\phi_1(\phi_2, s_1, s_2)$ (into $\phi_2(\phi_1, s_1, s_2)$ is also Ok), one can draw the phase diagram for I-N phase transition in the 3-D form like Fig. 2 (a) in the main text. As discussed in the main text, s_2 is calculated as a function of s_1, which is given by

$$s_2 = \frac{\psi^{\frac{1}{\varepsilon(1-\lambda_1)}} - \psi^{\frac{\lambda_1}{1-\lambda_1}}}{\psi^{\frac{1}{\varepsilon(1-\lambda_1)}} + 2\psi^{\frac{\lambda_1}{1-\lambda_1}}} \qquad (S22)$$

where $\psi = (1 + 2s_1)/(1 - s_1)$. Fig. S1 shows the profiles of s_2 for variable aspect ratio λ_1. One can see that s_2 could be approximately equal to s_1 with increasing λ_1. In the present problem, we process s_2 by using Eq. (S22) for the chosen parameters λ_1=10 and ε=0.4 (λ_2=4) in our calculations (a treatment of s_2=s_1 was considered in the previous theory [4]). As shown in the inset, the transient of s_1 and s_2 from zero to non-zero rapidly occurs at the same position, which means that the I-N phase transition in the bulk solution can be described by one of them. Here we use s_1 for discussions.

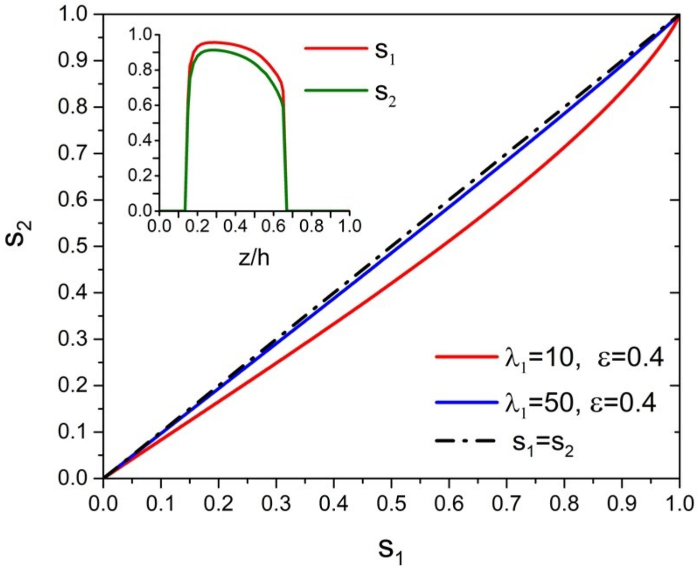

Fig. S1. Nematic order s_2 varies as a function of s_1 for variable aspect ratio. The inset shows the profiles of s_1 and s_2 in equilibrium calculated for ϕ_{01}=0.15, ϕ_{02}=0.1, and Pe_1=20.

3.2. Phase diagram in the ϕ_1-ϕ_2 space.

By solving Eq. (S21) under the consideration of Eq. (S22), we can show that s_1 varies in dependence on the concentration ϕ_1 and ϕ_2, which is draw for the phase diagram of I-N phase transition (the Fig. 2 (a) in the main text). In Fig. S2 (a), we show the phase diagram of I-N transition in the ϕ_1-ϕ_2 plane. The red dashed line as we can see indicates the stability limit of I phase, and we can prove it a straight line. By solving Eq. (S21), we can write down ϕ_1 as a function of ϕ_2 with the expression as $\phi_1 = k\phi_2 + \phi_1^*$. The prefactor $k = \omega(1 - \varepsilon\lambda_1)/(\lambda_1 - 1)$ where the weight ω is a constant conducted by $\lim_{s_1 \to 0} s_2/s_1$=0.8333, and ϕ_1^* is a constant depending on λ_1, thereby such function is linear, i.e., the dashed line is a straight line with $k = -0.2777$ and ϕ_1^*=0.1852 (λ_1=10 and ε=0.4).

However, we chose the solid line that indicates the stability limit of N phase shown in Fig. S2 (a) as the boundary line for I-N phase transition. This solid curve is drawn by connecting the two points which signify the critical concentration of I-N transition for thin $\phi_{c,1}$=0.1694 and thick $\phi_{c,2}$=0.6104 platelets seen in Fig. S2 (b). Apparently, this solid line is much approximate to the dashed line since their difference is rather small and they have the similar slope $k = -0.277$.

Therefore, in Fig. S2 (a), the triangle area (Gray) characterized by the solid line denotes the isotropic phase (s_1=0), and anywhere out of this region (Orange) signifies the nematic phase ($s_1 \neq 0$). Fig. S2 (b) shows the concentration-dependent nematic order parameter for the pure system of thin platelets (Purple) and thick platelets (Orange), respectively.

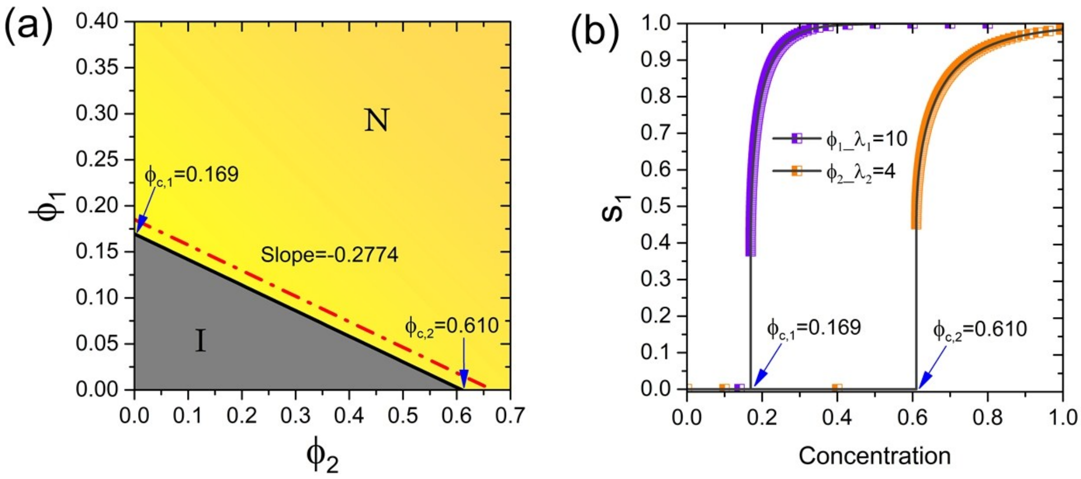

Fig. S2. (a) Phase diagram for I-N phase transition in the ϕ_1-ϕ_2 plane. The red dashed line is shown as stable-I-phase line and the black solid line is shown as stable-N-phase line. (b) The nematic order parameter s_1 is concentration-dependent for the pure system of thin platelets (Purple) and thick platelets (Orange), respectively. The arrows guide the critical concentration of I-N transition for both species of platelets.

References

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