

# Interplay between columnar and smectic stability in suspensions of polydisperse colloidal platelets

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The phase behavior of a model suspension of colloidal polydisperse platelets is studied using density-functional theory<sup>1</sup>. Platelets are modelled as parallel rectangular prisms of square section  $l$  and height  $h$ , with length and height distributions given by different polydispersities  $\delta_l$  and  $\delta_h$ . The model is intended to qualitatively represent the experimental colloidal platelet suspensions at high densities with highly degree of orientational ordering. These colloidal platelets have been synthesised by different techniques, but they can never be produced with uniform size; therefore, they possess an intrinsic polydispersity both in thickness and lateral size. Size polydispersity is known to greatly modify the phase behaviour of colloidal suspensions, since phases with (partial or full) spatial order cannot easily form: particles cannot accommodate into regular periodic structures due to the disparity in size. When two polydispersities come into play, the final structure delicately depends on their values, and order will develop along the less-frustrated spatial dimension(s).

With our theory, we can obtain the phase behavior of the model colloidal suspension, including nematic (N), smectic (S) and columnar (C) phases and its dependence with the two polydispersities  $\delta_l$  and  $\delta_h$ . When  $\delta_l > \delta_h$  we observe that the smectic phase stabilises first with respect to the columnar. If  $\delta_h > \delta_l$  we observe the opposite behavior. Other more complicated cases occur, e.g. the smectic stabilises from the nematic first but then there exists a first-order transition to the columnar phase. Our model assumes plate-rod symmetry, but the regions of stability of smectic and columnar phases are non-symmetric in the  $\delta_l - \delta_h$  plane due to the different dimensionality of ordering in the two phases. Microsegregation effects, i.e. different spatial distribution for different sizes within the periodic cell, take place in both phases. The theory confirms the stabilities of C and S phases as found in experiments on colloidal suspensions of mineral anisotropic particles (see figure)<sup>2-4</sup>.

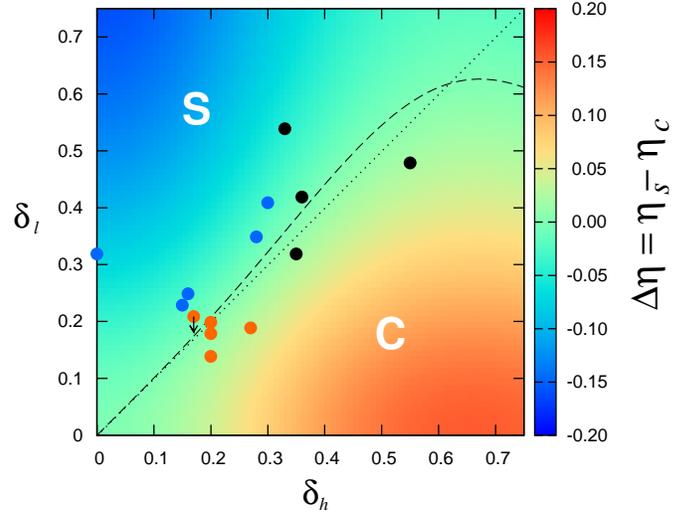


FIG. 1. Difference  $\Delta\eta = \eta_s - \eta_c$  of packing fractions of bifurcated S and C phases as a function of polydispersities  $\delta_l$  and  $\delta_h$ , in false colour. Dashed line corresponds to the curve  $\Delta\eta = 0$  (S and C phases bifurcate at the same packing fraction). The S (C) label indicates the region where the S (C) phase bifurcates from the N first. Dotted line is the bisectrice  $\delta_l = \delta_h$ . Orange, blue and black filled circles correspond to experiments where C, S and C+S are found. In the case of black circles and the orange circle with a down arrow, polydispersities correspond to those of the parent phase.

<sup>1</sup> E. Velasco and Y. Martínez-Ratón, *Phys. Chem. Chem. Phys.* **16**, 765 (2014).

<sup>2</sup> F. M. van der Kooij, K. Kassapidou, and H. N. W. Lekkerkerker, *Nature* **406**, 868 (2000).

<sup>3</sup> F. M. van der Kooij and H. N. W. Lekkerkerker, *Phys. Rev. Lett.* **84**, 781 (2000).

<sup>4</sup> J. G. Vroege, D. M. E. Thies-Weesie, A. V. Petukhov, B. J. Lemaire and P. Davidson, *Advanced Materials* **18**, 2565 (2006).