

## **INVITED ARTICLE**

## Multiphase coexistence in mixed suspensions of large and small hard platelets

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The phase behaviour of mixed suspensions of large and small hard platelets is treated by osmotic equilibrium theory. Depending on the size ratios of the small and large platelets, three distinct phase behaviour scenarios appear: isotropic–isotropic– nematic, isotropic–nematic and isotropic–nematic–nematic coexistence regions, in agreement with computer simulations. The experimental multiphase coexistence observed in mixed suspensions of large Titanate platelets and small Laponite platelets can be reproduced semi-quantitatively using osmotic equilibrium theory calculations.

Keywords: colloids; platelets; depletion; phase behaviour; liquid crystals

#### 1. Introduction

The understanding of the structure and phase behaviour of concentrated suspensions of colloidal particles has profited enormously from the developments in the theory of liquids [1-3]. Jean-Pierre Hansen made outstanding contributions to the field of liquid-state theory [4,5], but he also has a keen interest in the application of liquid-state theory to complex fluids [6] and colloidal suspensions [7,8].

In the last decades, phase transitions in colloidal suspensions induced by the addition of nonadsorbing polymers through the depletion interaction [9-11] have attracted significant attention (for recent reviews, see [12,13]). Also, in this field, Jean-Pierre Hansen made seminal contributions [14-21]. Traditionally, depletion-mediated phase transitions in colloidal suspensions have been realised often by adding nonadsorbing polymers. Adding small nonadsorbing colloidal solid particles may, however, also give rise to phase transitions [12]. The effects of polymers and small colloidal particles on the liquid crystal phase behaviour of suspensions of rod-like particles have been studied in the last few decades with the focus on rod-like colloids (for an overview, see Chapter 6 in [12]). It has been demonstrated that polymeric depletants have a significant impact on the liquid crystal phase behaviour of suspensions of anisometric particles [12,22-24]. The study of the effect of solid particles as depletants on the liquid crystal phase behaviour of suspensions of plate-like particles is of more recent date. Luan et al. [25], Kleshchanok et al. [26] and Doshi et al. [27,28] experimentally studied the phase stability of colloidal platelet–polymer mixtures and colloidal platelet–sphere mixtures, observing rich and interesting phase behaviour. Bates and Frenkel [29] and Zhang *et al.* [30,31] theoretically studied the phase stability of colloidal platelets and nonadsorbing polymer.

Rod-like particles are very efficient depletants [10,32,33]. A study of Bates and Frenkel [29] on the effect of (infinitely thin) rods as depletion agents in suspensions of colloidal platelets revealed that these rods affect the phase behaviour already at extremely small concentrations. Recently, it has also been observed that small platelets as depletants may be very effective [34,35] in inducing phase transitions at volume fractions as low as  $10^{-6}$  of thin platelets of the synthetic clay Laponite [36-39]. In fact, already more than 10 years ago, Rowan and Hansen [40] presented theoretical evidence for depletion-induced phase separation in binary mixtures of hard platelets. Thermodynamics and phase behaviour of binary mixtures of lamellar colloids were studied by Harnau, Rowan and Hansen [41] within a generalisation of the Zwanzig model for rods [42]. whereby the square cuboids can take only three orientations along the x, y or z axes. For certain length and diameter ratios of the lamellar colloids, their study reveals phase coexistence between an isotropic phase and two nematic phases of different compositions. Experimentally, such a phase behaviour scenario was indeed observed in mixtures of Titanate and Laponite by Nakato et al. [35].

In this paper, we formulate and apply osmotic equilibrium or free volume theory [12,30,31] to mixtures of large

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and small hard platelets. Three phase behaviour scenarios are observed: (1) only I-N coexistence, (2) I<sub>1</sub>-I<sub>2</sub>-N three phase coexistence plus I-N coexistence and (3) I-N plus  $I-N_1-N_2$  coexistence. Though not focused on here,  $I_1-I_2$ (scenario (2)) and  $N_1$ - $N_2$  (scenario (3)) coexistence regions appear as well. We determine the length to diameter ratios of the large and small platelets for which these scenarios occur. Our results are in agreement with those of Harnau et al. [41]. Subsequently, calculations are performed for length to diameter ratios of the large and small platelets, corresponding to the experimental values in the system studied by Nakato et al. [35]. The Titanate-Laponite mixture they studied is highly polydisperse, leading to a significant broadening [43] of the I-N coexistence region for the pure system of Titanate platelets. Nevertheless, satisfactory agreement is found for the concentration of small platelets to induce I-N1-N2 three-phase coexistence.

#### 2. Theory

## 2.1. Onsager–Parsons–Lee theory for the isotropic–nematic phase transition of hard platelets

We consider a dispersion of N hard cylindrical platelets with a diameter D and a thickness L in a volume V. The volume of a platelet  $v = \pi D^2 L/4$  and the volume fraction of platelets is given by  $\phi = Nv/V$ .

While the classic Onsager theory [44,45] for the isotropic–nematic phase transition in suspensions of rodlike particles also enables to make semi-quantitative predictions for the isotropic–nematic phase transition in suspensions of plate-like particles, the intrinsic difficulty with platelets, as pointed out by Onsager in his original paper, is that the contributions of third and higher order virial coefficients can no longer be neglected [46] as for long thin rods. For a recent overview to extend Onsager's second virial theory, see Harnau [47]. Here, we follow refs. [48,49] and write the Helmholtz free energy F within the Onsager–Parsons–Lee approach [50–52] as

$$\frac{\widetilde{F}}{\phi} = \ln \phi - 1 + \sigma[f] + \frac{2}{\pi} \frac{D}{L} \phi \, G_P(\phi) \langle \langle \Theta_{\text{ex}}(\gamma) \rangle \rangle,$$
(1)

where a constant term has been omitted which does not play a role in the calculation of the phase behaviour. Here,  $\tilde{F} = Fv/k_BTV$ . The orientational entropy of the platelets  $\sigma[f]$  in Equation (1) is defined as

$$\sigma[f] = \int d\Omega f(\Omega) \ln[4\pi f(\Omega)], \qquad (2)$$

with  $d\Omega$  an infinitesimal surface element on the unit sphere. The orientation distribution function (ODF) is normalised according to

$$\int d\Omega f(\Omega) = 1. \tag{3}$$

In Equation (1),  $\Theta_{ex}(\gamma)$  is the excluded volume divided by  $D^3$  between two platelets at fixed inter-particle angle  $\gamma$ :

$$\Theta_{\text{ex}}(\gamma) = \frac{\pi}{2} |\sin(\gamma)| + \frac{L}{D} \left\{ \frac{\pi}{2} + 2E[\sin(\gamma)] + \frac{\pi}{2} \cos(\gamma) \right\} + 2 \left( \frac{L}{D} \right)^2 |\sin(\gamma)|, \quad (4)$$

including the complete elliptic integral of the second kind E[x]. In Equation (1),  $\langle \langle \Theta_{ex}(\gamma) \rangle \rangle$  is defined as

$$\langle\langle \Theta_{\rm ex}(\gamma) \rangle\rangle = \int \int d\Omega d\Omega' f(\Omega) f(\Omega') \Theta_{\rm ex}(\gamma).$$
 (5)

The effects of higher order virial terms are incorporated via the Parsons–Lee scaling factor  $G_P$ :

$$G_P(\phi) = \frac{4 - 3\phi}{4(1 - \phi)^2},$$
 (6)

The factor  $G_P$  ensures that the ratios of the third and higher virial coefficients to the second virial coefficient are the same as for hard spheres.

At low concentrations, the system is isotropic (I), i.e. all platelets are oriented randomly and  $f^{I} = 1/4\pi$ , so that  $\sigma^{I} = 0$  and  $\Theta_{ex}^{I} = \langle \langle \Theta_{ex}(\gamma) \rangle \rangle$  becomes

$$\Theta_{\text{ex}}^{I} \approx \frac{\pi^2}{8} + \frac{L}{D} \left( \frac{3\pi}{4} + \frac{\pi^2}{4} \right), \tag{7}$$

where a term of order  $(L/D)^2$  has been omitted in the excluded volume term (here, the focus is on thin  $(L/D \ll 1)$  platelets).

Hence, the free energy in the isotropic phase within the Parsons–Lee approximation reads

$$\frac{\widetilde{F}^{I}}{\phi} = \ln \phi - 1 + \frac{2}{\pi} \frac{D}{L} G_{P}(\phi) \Theta_{\text{ex}}^{I}, \qquad (8)$$

Standard thermodynamics directly provides the (dimensionless) osmotic pressure  $\tilde{P} = Pv/k_BT$  and chemical potential  $\tilde{\mu} = \mu/k_BT$  of the platelets in suspension

$$\widetilde{P}^{I} = \phi + \frac{2}{\pi} \phi^{2} \frac{D}{L} \frac{1 - (1/2)\phi}{(1 - \phi)^{3}} \Theta_{\text{ex}}^{I}, \qquad (9)$$

and

$$\widetilde{\mu}^{I} = \ln \phi + \frac{2}{\pi} \frac{D}{L} \frac{8\phi - 9\phi^{2} + 3\phi^{3}}{4(1-\phi)^{3}} \Theta^{I}_{\text{ex}}.$$
 (10)

via the chemical potential in a canonical system  $\mu = (\partial F/\partial N)_{V,T}$  or  $\tilde{\mu} = (\partial \tilde{F}/\partial \phi)_{V,T}$  and the osmotic pressure  $P = -(\partial F/\partial V)_{N,T}$  or  $\tilde{P} = \phi \tilde{\mu} - \tilde{F}$ .

Above a certain concentration, the platelets spontaneously assume a preferred orientation, the nematic state. One may then compute the ODF at each concentration numerically by minimising the Helmholtz free energy expression (1), while using the condition of Equation (3). Since the nematic phases we consider are uniaxial in symmetry, the solid angle  $\Omega$  only depends on the polar angle  $\theta$  between a nematic director and the orientation of the platelet. Given the fact that a functional free energy minimisation is technically involved (see for instance [53,54]), we resort to a much simpler analytical approach based on Odijk's Gaussian approximation for the ODF  $f(\theta)$  [55]

$$f_G(\theta) \sim \frac{\alpha}{4\pi} \exp\left[-\frac{1}{2}\alpha\theta^2\right],$$
 (11)

that applies to angles  $-\pi/2 \le \theta \le \pi/2$ . The prefactor of the Gaussian ODF follows from Equation (3).

Using the Gaussian ODF in the free energy of the nematic state, we obtain

$$\frac{\widetilde{F}^{N}}{\phi} \sim \ln \phi - 1 + \ln \alpha - 1 + \phi G_{P}(\phi) \left[ \frac{D}{L} \sqrt{\frac{\pi}{\alpha}} + 4 \right],$$
(12)

where we have used that to leading order  $\sigma^N \sim \ln \alpha - 1$ , hence [54]

$$\Theta_{\text{ex}}^{N} = \langle \langle \Theta_{\text{ex}}(\gamma) \rangle \rangle^{N} \sim 2\pi \frac{L}{D} + \frac{\pi}{2} \sqrt{\frac{\pi}{\alpha}}.$$
 (13)

The chemical potential and osmotic pressure in the nematic state can now easily be obtained

$$\widetilde{\mu}^N \sim \ln \phi + \ln \alpha - 1 + \frac{8\phi - 9\phi^2 + 3\phi^3}{4(1-\phi)^3} \left[\frac{D}{L}\sqrt{\frac{\pi}{\alpha}} + 4\right],$$
(14)

and

$$\widetilde{P}^{N} \sim \phi + \phi^{2} \frac{1 - (1/2)\phi}{(1 - \phi)^{3}} \left[ \frac{D}{L} \sqrt{\frac{\pi}{\alpha}} + 4 \right].$$
(15)

The free energy and various thermodynamic properties can be calculated explicitly once the unknown variational parameter  $\alpha$  is determined. This parameter follows from the minimisation

$$\frac{\partial F}{\partial \alpha} = 0. \tag{16}$$

Applying this to Equation (12) yields

$$\alpha \sim \frac{\pi}{4} \left(\frac{D}{L}\right)^2 \phi^2 G_P^2(\phi), \qquad (17)$$

Insertion of this result into Equation (12) provides the expression [54]

$$\frac{\widetilde{F}^{N}}{\phi} \sim (\ln \phi - 1) + \left[ 2 \ln \left( \frac{D}{L} \frac{\sqrt{\pi}}{2} \phi G_{P}(\phi) \right) - 1 \right] + \left[ 4 \phi G_{P}(\phi) + 2 \right], \quad (18)$$

for the Helmholtz energy and

$$\widetilde{P}^N \sim \phi + \frac{2\phi - \phi^2}{(1 - (3/4)\phi)(1 - \phi)} + \frac{4\phi^2 - 2\phi^3}{(1 - \phi)^3},$$
 (19)

and

$$\widetilde{\mu}^{N} \sim 1 + 2\ln\left(\frac{D}{L}\frac{\sqrt{\pi}}{2}\right) + \ln\phi + 2\ln[\phi G_{P}(\phi)] \\ + 4\phi G_{P}(\phi) + \frac{2-\phi}{(1-(3/4)\phi)(1-\phi)} \\ + \frac{4\phi - 2\phi^{2}}{(1-\phi)^{3}},$$
(20)

for the osmotic pressure and chemical potential, respectively. It is now possible to compute the coexisting isotropic and nematic concentrations of hard platelets within the Parsons–Lee approximation using the Gaussian form for the ODF (GODF). In general, coexisting binodal concentrations follow from solving the concentrations for which the chemical potentials  $\mu$  and osmotic pressures *P* in phases *i* and *ii* are equal

$$\widetilde{\mu}^{i} = \widetilde{\mu}^{ii}$$
$$\widetilde{P}^{i} = \widetilde{P}^{ii}, \qquad (21)$$

where *i* and *ii* used can be used for any of the isotropic (I) or nematic (N) phases. Results for the binodal isotropic and nematic concentrations using the Parsons–Lee approximation (curves) are shown in Figure 1 as a function of L/D. Minimisation of the free energy using a Gaussian form of the ODF (dotted curves) is compared to minimising the free energy while solving the ODF numerically (solid curves) and to computer simulation results (data points).

It is clear that the Gaussian approximation predicts a wider coexistence region and slightly higher coexisting concentrations, especially on the nematic side. These findings are similar to the situation for the I-N phase transition of hard rod-like particles [12,23]. Still, given the relatively simple approach, the Gaussian ODF combined with the Parsons-Lee approximation provides a quite reasonable description for the I-N phase transition of hard platelets, except for  $L/D \rightarrow 0$ . Next, mixtures of large (and thin) hard platelets and small (and thin) hard platelets are considered. Then, depletion forces modify the phase behaviour of a system consisting of only hard monodisperse platelets. In case of depletion-induced attractions, the particles become



Figure 1. I-N coexistence for pure hard platelets. Platelet concentration is given in terms of the quantity  $c = ND^3/V= \phi(4/\pi)D/L$ . Curves are theoretical predictions using the Parsons– Lee (P-L) approximation combined with a numerical minimisation (solid curves) and minimisation using the Gaussian approximation to the ODF (dotted curves). Data points are computer simulation results by (1) Veerman and Fenkel [56] for L/D = 1/10 giving  $c^I$ = 3.82 and  $c^N = 3.87$ , (2) Zhang *et al.* [30] for L/D = 1/10 corresponding to  $c^I = 4.03$  and  $c^N = 4.17$  and for L/D = 1/20 :  $c^I = 3.90$ and  $c^N = 4.17$ , (3) Van der Beek *et al.* [57] for L/D = 1/15:  $c^I =$ 3.86 and  $c^N = 4.11$  and (4) Eppenga and Frenkel [58] for L/D =0:  $c^I = 4.04$  and  $c^N = 4.12$ . It is noted that in the computer simulations, cut spheres were used to model platelets, which slightly differs from the theoretical description of cylindrical platelets used within osmotic equilibrium theory in this work.

much more aligned and the Gaussian approximation becomes more accurate with increasing amount of depletant [23].

# 2.2. Free volume theory for the phase behaviour of a mixture of large and small platelets

We use free-volume theory (FVT) to compute the phase behaviour of a suspension large thin hard platelets with diameter  $D_1$  and thickness  $L_1$  of volume fraction  $\phi_1$  dispersions mixed with small thin hard platelets with diameter  $D_2$ and thickness  $L_2$  of volume fraction  $\phi_2$ . The volumes of the platelets 1 and 2 are  $v_1 = (\pi/4)D_1^2L_1$  and  $v_2 = (\pi/4)D_2^2L_2$ and the relative sizes are defined by the ratios r, q and t

$$r = \frac{L_1}{D_1}, \quad q = \frac{D_2}{D_1}, \quad t = \frac{L_2}{L_1},$$

so  $L_2/D_2 = rt/q$ .

Free volume or osmotic equilibrium theory for suspensions of mixed colloid–polymer suspensions and mixtures of large and small colloids [12,59,60] makes use of placing the system of interest in osmotic equilibrium with a hypothetical reservoir, which only contains the polymers or small colloids. Here, we place the large platelets (coded #1) and small platelets (coded #2) in the system while the reservoir only contains small platelets. The semi-grand canonical free energy  $\Omega$  for a disperse mixture of platelets having a volume V can then be written as

$$\Omega(N_1, V, \mu_2) = F_0(N_1, V, \mu_2 = -\infty) + \int_{-\infty}^{\mu_2} d\mu_2' \left(\frac{\partial \Omega(N_1, V, \mu_2')}{\partial \mu_2'}\right)$$
(22)

where  $F_0$  is the Helmholtz free energy of the dispersion of pure (large) hard platelets,  $\mu_2$  is the chemical potential of the small added platelets. We use the thermodynamic relation  $\partial \Omega / \partial \mu_2 = -N_2$ , where  $N_2$  is the averaged number of small platelets 2 in the system. Using the Widom particle insertion theorem [61], we can write

$$N_2 = n_2^R \langle V_{\text{free}} \rangle, \qquad (23)$$

where  $\langle V_{\text{free}} \rangle$  is the ensemble-average free volume for the small platelets in the system of large hard platelets and  $n_2^R$  is the number density of small hard platelets in the reservoir. We now make the key approximation to replace  $\langle V_{\text{free}} \rangle$  by the free volume in the pure hard platelet dispersion  $\langle V_{\text{free}} \rangle_0$ . Then,

$$N_2 = n_2^R \langle V_{\text{free}} \rangle_0. \tag{24}$$

This expression is correct in the limit of small depletant concentration but is only an approximation for higher depletant concentrations. Substituting the approximation (24) into (22) and using the Gibbs–Duhem relation,

$$n_2^R \mathrm{d}\mu_2 = \mathrm{d}P^R,\tag{25}$$

gives

$$\widetilde{\Omega} = \widetilde{F} - \frac{\chi}{q^2 t} \widetilde{P}_2^R, \qquad (26)$$

where  $\widetilde{P}_2^R = v_2 P_2^R / k_B T$  is the (osmotic) pressure of the small platelets in the reservoir,  $\chi$  is the free volume fraction of small platelets available in the system and  $\widetilde{\Omega} = \Omega v_1 / k_B T V$ . In case the concentration of the small platelets in the reservoir is given by Van 't Hoff's law, one can write  $\widetilde{P}_2^R = n_2^R v_2 = \phi_2^R$ .

The free volume fraction for small platelets 2 in a dispersion of large platelets 1 is derived here from scaled particle theory, in a similar fashion as for other colloidal mixtures and colloid–polymer mixtures [12,22,60]. According to the Widom insertion theorem, the free volume fraction  $\chi$  can be calculated from the reversible work *W* required for inserting a platelet 2 into the dispersion of platelets 1 via

$$\chi = \frac{\langle V_{\text{free}} \rangle_0}{V} = e^{-W/k_B T}.$$
 (27)

An expression for the work of insertion W can be obtained from scaled particle theory (SPT) [62]. This work W is calculated by expanding (scaling) the size of the particle to be inserted from zero to its final size: the size of the scaled particle is characterised by  $\lambda D_2$  and  $\nu L_2$ , with  $\lambda$  and  $\nu$  running from 0 to 1. In the limit  $\lambda$ ,  $\nu \rightarrow 0$ , the inserted platelet 2 approaches a point particle and it is unlikely that the excluded volumes of large and small particles overlap. Hence,

$$W = -k_B T \ln \left[1 - n_1 v_{\text{excl}}(\lambda, \nu)\right] \quad \text{for } \lambda, \nu \ll 1.$$
 (28)

The excluded volume between large and small platelets can be written as [45]

$$v_{\text{excl}} = \left(\frac{\pi}{4}\right)^2 D_1 \lambda D_2 (D_1 + \lambda D_2) + \left(\frac{\pi}{4}\right) (L_1 D_1^2 + \nu L_2 \lambda^2 D_2) + \left(\frac{\pi}{8}\right) (L_1 \lambda^2 D_2^2 + \nu L_2 D_1^2) + \left(\frac{\pi}{8}\right)^2 D_1 \lambda D_2 (L_1 + \nu L_2) + \left(\frac{\pi}{4}\right) L_1 \nu L_2 (D_1 + \lambda D_2).$$
(29)

The opposite limit  $\lambda$ ,  $\nu \gg 1$  corresponds to the case that the size of the inserted platelet is very large. Then, *W* is, to a good approximation, equal to the volume work needed to create a cavity of volume  $\frac{\pi}{4}\lambda^2 D_2^2\nu L_2$  and is given by

$$W = \frac{\pi}{4} \lambda^2 D_2^2 \nu L_2 P_0 \quad \text{for } \lambda, \nu \gg 1, \qquad (30)$$

where  $P_0$  is the (osmotic) pressure of the pure dispersion of large hard platelets. In SPT, the above two limiting cases are connected by expanding W given by Equation (28) as a series in  $\lambda$  and  $\nu$  up to quadratic order and combining it with W (30) for the cubic term. By setting  $\lambda = \nu = 1$ , one obtains the work to insert a small platelet 2 in a system of large platelets 1

$$\frac{W}{k_B T} = -\ln[1 - \phi_1] + A \frac{\phi_1}{1 - \phi_1} + B \left(\frac{\phi_1}{1 - \phi_1}\right)^2 + q^2 t \widetilde{P}_0,$$
(31)

where

$$A = \frac{\pi}{4} \frac{q}{r} + \frac{\pi}{2} q + \frac{1}{2}t + rt + \frac{\pi}{4} \frac{q^2}{r} + \frac{1}{2}q^2 + \frac{\pi}{2}qt + qtr \quad \text{and}$$
$$B = \frac{1}{2} \left(\frac{\pi}{4} \frac{q}{r} + \frac{\pi}{2}q + \frac{1}{2}t + rt\right)^2.$$

Using Equation (27), this yields for  $\chi$ 

$$\chi = (1 - \phi_1) \exp\left(-A \frac{\phi_1}{1 - \phi_1} - B \left(\frac{\phi_1}{1 - \phi_1}\right)^2 -q^2 t \widetilde{P}_0\right).$$
(32)

In order to calculate  $\chi$  in the isotropic phase, Equation (32) can be used straightforwardly. Strictly speaking, in the expression for  $\chi$  in Equation (32), the osmotic pressure of the pure platelets for  $\tilde{P}_0$  in the nematic phase should be used in order to compute  $\chi$  in the nematic phase(s). In order to simplify calculations, we follow the approximation introduced by Bolhuis *et al.* [63] in their treatment of the phase behaviour of rod-like colloids and nonadsorbing polymer and use for  $\tilde{P}_0$  the expression for isotropic phase, (9), for both the isotropic and the nematic phases.

The minimisation of  $\Omega$ 

$$\frac{\partial \Omega}{\partial \alpha} = 0. \tag{33}$$

with respect to the parameter  $\alpha$  then takes the form given by Equation (17).

The pressure and the chemical potential are now given by

$$\widetilde{P}^{I,N} = \widetilde{P}_0^{I,N} + \frac{\widetilde{P}^R}{q^2 t} \left( \chi - \phi_1 \frac{\partial \chi}{\partial \phi_1} \right), \qquad (34)$$

and

$$\widetilde{\mu}_{1}^{I,N} = \widetilde{\mu}_{1,0}^{I,N} - \frac{\widetilde{P}^{R}}{q^{2}t} \frac{\partial \chi}{\partial \phi_{1}}, \qquad (35)$$

For the chemical potentials and osmotic pressures of the pure plate systems 1, we use the analytical expressions given by Equations (9) and (10) for the (osmotic) pressure and chemical potential of the isotropic phase for the pure platelets and for the chemical potential and (osmotic) pressure of the nematic phase of pure platelets, Equations (19) and (20) are used. By setting equal both the chemical potentials and pressures, see Equation (21), we can compute isotropic–nematic coexistence curves for platelet mixtures. As it turns out, also I-I and N-N demixing curves appear depending on the values chosen for q, r and t.

#### 3. Results and discussion

We first consider different phase transition scenarios for our system of large and small platelets. In their study of the phase behaviour of infinitely thin plates and polymers, Bates and Frenkel [29] observed  $I_1$ - $I_2$ -N coexistence regions for a polymer size relative to platelet diameter larger than 0.3 and I- $N_1$ - $N_2$  coexistence for ratios smaller than 0.08, while (only) broadening of the I-N transition was detected for



Figure 2. Phase diagrams for mixtures of large (1) and small (2) platelets for various combinations of r, q and t values indicated above each diagram. Scenarios are shown for isotropic–nematic (I-N) phase coexistence (left panels), I-N, I<sub>1</sub>-I<sub>2</sub> and I<sub>1</sub>-I<sub>2</sub>-N coexistence (middle panels) and finally, for regions where besides I-N coexistence also N-N and I-N<sub>1</sub>-N<sub>2</sub> coexistence regions appear (right panels). Upper panels represent phase diagrams in terms of the reservoir small platelet osmotic pressure on the ordinate. Phase diagrams in system concentrations of small and large platelets are plotted in the lower panels. Critical I-I and N-N points are indicated by open circles.

size ratios in between these limits. Zhang *et al.* [30,31] observed  $I_1$ - $I_2$ -N phase transitions for similar size ratios and also considered  $N_1$ - $N_2$  coexistence, but such demixing was superseeded by the more highly ordered columnar crystal phase. While Harnau et al. [41] did not observe  $I_1$ - $I_2$ -N coexistence, they did detect I-N broadening as well as the  $N_1$ - $N_2$  coexistence using the Zwanzig model.

Using osmotic equilibrium or free volume theory outlined above, we performed calculations for three cases:

- *r*=0.04, *q*=0.3, *t*=0.75 (I-I and I-N were observed),
- r=0.04, q=0.2, t=0.5 (only I-N was observed) and
- r=0.01, q=0.08, t=1 (I-N and N-N were observed).

Parameters were chosen close to those reported by Harnau *et al.* [41]; numerics differ slightly but rather similar phase behaviour, N<sub>1</sub>-N<sub>2</sub> coexistence plus I-N broadening was found for r=0.01, q=0.08 and t=1. Representative free volume theory results are reported in Figure 2. These free volume theory results match with the three phase behaviour scenarios previously observed on platelet plus polymer mixtures. One may compare the two cases when realising the platelet diameter plays a similar role as the polymer diameter.

Nakato and co-workers [35] studied the liquid-crystal phase behaviour of suspensions of plate-like Titanate particles. These particles are characterised by a mean diameter of 7.1  $\mu$ m and a thickness of 0.75 nm, so D/L is close to 7500. The size distribution of these particles can be de-

scribed using a log-normal distribution with a width of 32.4%. The width of the biphasic I-N region ranges for this system from  $\phi_I \approx 3.7 \times 10^{-5}$  to  $\phi_N \approx 1.9 \times 10^{-3}$ , which indeed is indicative of a rather polydisperse system [43]. By adding very small amounts of laponite platelets, synthetic hectorites with a diameter of 30 nm and thickness of 1 nm [36-39,64], Nakato and co-workers [35] observed a triphasic I-N<sub>1</sub>-N<sub>2</sub> phase coexistence region when adding only 0.0005-0.005 g/L of Laponite, which corresponds to volume fractions  $2 \times 10^{-7} - 2 \times 10^{-6}$  (density of Laponite  $\approx$  2.53 g/mL). These striking observations at first glance seem mysterious. Free volume theory computations for the experimental conditions of Nakato et al. yield results that predict the presence of a triphasic I-N<sub>1</sub>-N<sub>2</sub> phase coexistence region when adding tiny amounts of small platelets, see Figure 3.

The computed three-phase triangle extends from  $\phi_2 \approx 5 \times 10^{-7} - 2 \times 10^{-6}$  at  $\phi_1$  from  $6 \times 10^{-4} - 20 \times 10^{-4}$ . The range in clay concentrations observed experimentally is much wider as for the monodisperse theoretical case which reveals the effect of polydispersity. It is clear, however, that free volume theory provides a reasonable prediction of the multiphase I-N<sub>1</sub>-N<sub>2</sub> coexistence region observed experimentally.

Justification for the use of FVT resides in the observation that very small volume fractions of depletant (small platelets) are needed to establish  $N_1$ - $N_2$  demixing and triphasic equilibria. One of the main approximations of FVT is that the depletant particles do not interact with each



Figure 3. Phase diagram for large and small hard platelets with r=1/7500, q=1/250, t=1 to model an experimental Titanate + Laponite mixture.

other and therefore, behave as an ideal gas. In view of the tiny volume fractions, this assumption seems appropriate for the present case.

The near-ideal gas behaviour of the depletant (very dilute) also justifies the assumption of isotropic order in the free-volume contributions (cf. Equation (32)). This is backed up by results from the full, self-consistent theory (not shown here) in which the depletant is allowed to order nematically. These results reveal that the degree of nematic order of the small platelets is very weak indeed so that isotropic order is warranted. On the contrary, the large platelets, in general, exhibit very strong nematic order (characterised by large values of  $\alpha$ ) which lends credence to the use of the asymptotic Gaussian form employed in this study.

The N<sub>1</sub>-N<sub>2</sub> phase separation observed experimentally by Nakato et al. [35] and reproduced here semiquantitatively using osmotic equilibrium theory calculations is on a fundamental level equivalent to the predicted expanded-to-condensed crystal transition for spherical colloids with a short-ranged attractive interaction [65–68]. Bolhuis and Frenkel [65] presented an intuitive argument for the latter transition: the decrease of the energy on compression will outweigh the loss of entropy that is caused by the decrease of the free volume. For the N<sub>1</sub>-N<sub>2</sub> transition of plate-like particles considered here, the same argument can in essence be applied, albeit with a subtle modification. As was shown by Vroege and Lekkerkerker [43] for the N<sub>1</sub>-N<sub>2</sub> transition in a dispersion of bidisperse rod-like particles, the excluded volume per particle is the same in the two coexisting nematics as the higher density in dense nematic leads to a higher degree of ordering, compensating the increased concentration which is also the case here. The higher density nematic, however, loses more orientational entropy which is compensated by a larger attractive depletion attraction. A similar mechanism is at play in systems of attractive rod-like mesogens as has been demonstrated in a number of theoretical studies [69,70].

What makes the observation of Nakato *et al.* [35] of two coexisting nematics under the influence of the depletion attraction of a small depletant extra relevant is that it presents the first experimental example of two coexisting isostructural ordered phases under the influence of the depletion attraction. Frenkel and co-workers [65,66] predicted that this could happen in a system of spheres but so far this has not observed. Hence, the work of Nakato *et al.* [35] adds another example of the richness of suspensions of anisometric particles.

#### 4. Concluding remarks

In this work, we applied free volume theory to a mixture of large and small hard platelets. It is shown that besides the isotropic (I)–nematic (N) phase transition region,  $I_1$ - $I_2$  and  $N_1$ - $N_2$  coexistence regions appear by changing the relative sizes of the large and small platelets. The advantage of free volume theory is that it allows an easy route to construct phase diagrams in the terms of the concentrations of both components in the system of interest. These results demonstrate that it is possible to induce N-N coexistence regions when adding tiny amounts of small platelets to a dispersion of large platelets as was also found experimentally in Titanate–Laponite mixtures.

The addition of Laponite in equal amounts to the smectite clay Montmorillonite leads to the formation of gel networks [71–73]. Our calculations further indicate the possibility to observe interesting multiphase coexistence in mixed suspensions of the smectic clay Beidellite (which displays a nematic liquid crystal phase, see ref. [74]), and low Laponite concentrations ( $\phi \approx 4 \times 10^{-4}$ , corresponding to 1 g/L).

In conclusion, the area opened up by Hansen and coworkers of small and large platelet mixtures offers intriguing opportunities to observe interesting depletion-induced phase behaviour and at the same time presents significant scientific challenges.

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#### **Disclosure statement**

No potential conflict of interest was reported by the authors.

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