2
Isotropic-nematic density inversion in mixtures of thin and thick hard platelets

Abstract
We study the phase behaviour of a binary mixture of thin and thick hard platelets, using Onsager’s second virial theory for binary mixtures in the Gaussian approximation. Higher virial terms are included indirectly by means of a rescaling of the free energy (Parsons’ approach). Our calculations provide a simple explanation for the isotropic-nematic density inversion, as experimentally observed in systems of polydisperse gibbsite platelets by Van der Kooij [60]. In these systems, a nematic upper phase was found to coexist with an isotropic bottom phase. We confirm the original conjecture of the authors, which states that the phenomenon originates from a pronounced fractionation in thickness between the phases, such that the thick platelets are largely expelled from the nematic phase and preferentially occupy the isotropic phase. Our calculations show that the inverted state is found in a major part of the I − N coexistence region. We also locate a nematic-nematic demixing transition for any thickness ratio $L_2/L_1 > 1$. At small ratios, the N − N coexistence region is bounded by a lower critical point which shifts towards lower osmotic pressures as the thickness ratio is increased. At high ratios ($L_2/L_1 > 3.3$), a triphasic coexistence is encountered at which two nematic phases coexist with an isotropic phase. We show that the demixing transition is driven by a small $O(L/D)$-contribution to the excluded volume entropy.

2.1. Introduction
Contrary to dispersions of colloidal rods, there is little experimental evidence of the isotropic-to-nematic phase transition in systems of platelike colloids. The first observations date back to 1938 in aqueous suspensions of clay particles by Langmuir [2]. However, many later observations in other clay systems have been obscured by gelation effects. In particular, macroscopic phase separation seems to be inhibited by the formation of a rigid gel network [61,62]. Recently, a novel model system for platelike colloids has been developed, consisting of sterically stabilized gibbsite platelets [11]. This system unambiguously shows a macroscopic phase separation into an isotropic and a birefringent nematic phase. The densities of these phases are in reasonable agreement with computer simulation results for hard platelets [63,64].

An important feature of the gibbsite platelets is their polydispersity, i.e. the particles differ in size and shape. The influence of polydispersity on the phase behaviour of
rod- and platelike colloids is an important factor in the interpretation of experimental results, as already pointed out by Onsager in his original paper [21]. Calculations on binary mixtures of long and short rods [65] within Onsager’s approach have revealed some interesting phenomena like the fractionation effect (with the longer rods going preferentially to the nematic phase), a widening of the biphasic gap, a reentrant phenomenon and the possibility of triphasic and nematic-nematic equilibria [66].

The gibbsite systems, developed by Wierenga et al. [9], display a very broad size distribution in both diameter and thickness. The polydispersity \( \sigma \) was found to be approximately 25% for both diameter and thickness [11]. Until recently, the effect of polydispersity in the platelets’ thickness was considered to be far less important than the polydispersity in diameter, since the thickness hardly contributes to the excluded volume between two platelets and thus cannot have a significant influence on the phase behaviour. However, a recent experimental study by van der Kooij et al. [60] has shown that polydispersity in thickness can have considerable implications for the phase behaviour of platelike colloids.

In these experiments, the phase behaviour of suspensions of gibbsite platelets with a particularly broad distribution in thickness was investigated [60]. The polydispersity in thickness, although difficult to determine accurately, was estimated to be about 50%. The high polydispersity is caused by the presence of a significant number of very thick platelets, as observed on the transmission electron microscopy (TEM) micrograph of the gibbsite samples. The suspensions show an \( I - N \) phase separation over a wide range of particle concentrations. However, a remarkable phenomenon was observed;
in a major part of the coexistence region a nematic upper phase was found to coexist with an isotropic bottom phase (Fig. 2.1), which implies that the nematic phase has a lower mass density than the coexisting isotropic phase. Henceforth, we will refer to this phenomenon as the $I - N$ density inversion. It is argued that this anomalous behaviour is related to the platelets’ considerable polydispersity in thickness. To explain the underlying mechanism, two aspects are mentioned by the authors [60]. On the one hand, the difference between the number densities of the coexisting phases; the total number density of platelets in the nematic phase will in general be higher than that in the coexisting isotropic phase and, consequently, the nematic phase will be more dense than the isotropic phase. On the other hand there is a clear evidence of fractionation in thickness between the coexisting phases, such that the thick platelets (i.e. the largest particles) accumulate in the isotropic phase, thereby increasing the mass density of the isotropic phase relative to that of the nematic phase. The authors conjecture that an $I - N$ density inversion may occur if the fractionation effect is strong enough to overcome the difference between the number densities of the coexisting phases.

Our objective in this Chapter is to study the phase behaviour of a simple binary mixture of thin and thick hard platelets starting from Onsager’s theory. We show that our calculations indeed account for a significant fractionation effect as well as a density inversion in the $I - N$ coexistence region, thus confirming the conjecture of van der Kooij et al.

Within our theoretical approach, we also locate a nematic-nematic demixing transition. We show that a stable demixing transition occurs irrespective of the thickness ratio. At high ratios, an associated triphasic equilibrium is found. Recently, a similar demixing transition was found in binary mixtures of thin and thick rods [67–69], although only at sufficiently high thickness ratios ($\gtrsim 4$). There, even a stable isotropic-isotropic demixing transition could be located (see also [70]). This issue will be discussed in Chapter 5.

2.2. Onsager formulation

We consider a binary mixture of hard platelets of species $j = 1, 2$ with length (thickness) $L_j$ and common diameter $D$ in a macroscopic volume $V$. For the sake of definiteness we denote the thicker platelets by subscript 2, so that the composition variable $x = N_2/(N_1 + N_2)$ is the mole fraction of the thick platelets. Note that, contrary to a slender rod, the length-to-diameter ratio $L/D$ of a thin platelet is a small parameter.

A nematic phase in a dilute solution of platelets is characterized by an ODF, $f_j(\theta)$, describing the distribution of the polar angle $\theta$ between the normal to the platelet of type $j$ and the nematic director. The ODF must be normalized according to $\int f_j(\Omega) d\Omega \equiv 1$, with $\Omega$ the solid angle of the platelet’s normal vector.

The formation of an isotropic state (with $f_j$ constant) or a nematic state (with $f_j$ a peaked distribution) is caused by a competition between orientational entropy (favouring the isotropic state) and the excluded volume entropy (favouring the nematic state). Onsager [21] defined the quantity $\sigma_j$ as a measure for the (negative of the)
2. Density inversion in mixtures of thin and thick hard platelets

orontional entropy

$$\sigma_j \equiv \int f_j(\theta) \ln[4\pi f_j(\theta)]d\Omega, \quad j = 1, 2,$$

which has its minimum ($\sigma_j = 0$) in the isotropic state, whereas $\sigma_j > 0$ in the nematic state. In the second virial approximation, the interactions between hard particles are expressed as an excluded volume entropy depending on the orientation-dependent excluded volume between two particles. The excluded volume between two platelets (i.e. circular disks) with thicknesses $L_j$ and $L_k$ as a function of their mutual angle $\gamma$ is given by

$$v_{\text{excl}}^{jk}(\gamma) = \frac{\pi}{2} D^3 \sin \gamma + (L_j + L_k) D^2 \left\{ \frac{\pi}{4} + E(\sin \gamma) + \frac{\pi}{4} |\cos \gamma| \right\} + \mathcal{O}(L^2 D),$$

where $E(k)$ is the complete elliptic integral of the second kind. Note that the leading order term does not depend on the thickness so that the $\mathcal{O}(L/D)$-term must be included to account for different plate thicknesses. In the isotropic phase, the excluded volume can be readily calculated using the isotropic averages $\langle\langle \sin \gamma \rangle\rangle_{\text{iso}} = \pi/4$ and $\langle\langle E(\sin \gamma) \rangle\rangle_{\text{iso}} = \pi^2/8$ [21]

$$v_{\text{excl,iso}}^{jk} = \frac{\pi^2}{8} D^3 + (L_j + L_k) D^2 \left\{ \frac{\pi^2}{8} + \frac{3\pi}{8} \right\} + \mathcal{O}(L^2 D).$$

A measure for the average excluded volume interaction between platelets of type $j$ and $k$ is given by the average of its angular dependence [21]

$$\rho_{jk} \equiv \iint \frac{v_{\text{excl}}^{jk}(\gamma)}{v_{\text{excl,iso}}^{0}} f_j(\theta) f_k(\theta') d\Omega d\Omega', \quad (2.4)$$

with $v_{\text{excl,iso}}^{0} = D^3 \pi^2/8$, the average excluded volume between two randomly orientated platelets with zero thickness. Substituting Eq. (2.3) into Eq. (2.4) yields for the isotropic phase

$$\rho_{jk}^{\text{iso}} = 1 + \frac{L_j + L_k}{D} \left( 1 + \frac{3}{\pi} \right) + \mathcal{O}(L^2 / D^2).$$

where the second contribution is of the order $L/D$ smaller than the leading order term. The total Helmholtz free energy (in units $k_B T$ per particle) of a binary mixture within the second virial approximation can now be expressed in terms of $\sigma_j$ and $\rho_{jk}$

$$\frac{\beta F}{N} \sim \text{cst} - 1 + \ln c + (1 - x) \ln(1 - x) + x \ln x + (1 - x)\sigma_1 + x \sigma_2$$

$$+ c \left[ (1 - x)^2 \rho_{11} + 2x(1 - x)\rho_{12} + x^2 \rho_{22} \right],$$

*The definition of $\rho_{jk}$ is slightly different from the one originally used by Onsager [21], since we only retain the leading order term $v_{\text{excl,iso}}^{0}$ in the denominator instead of the full expression Eq. (2.3). This leads to $\rho_{jk}^{\text{iso}} = 1 + \mathcal{O}(L/D)$ whereas in [21] $\rho_{jk}^{\text{iso}} \equiv 1$, by definition. Both definitions are equivalent up to leading order.*
equivlent to Eq. (1.25) for \( j = 1, 2 \). Here, \( c \) is the total number density of platelets rendered dimensionless by relating it to \( \nu_{\text{excl,iso}}^0 \) in the following way

\[
c = \frac{1}{2} \nu_{\text{excl,iso}}^0 \frac{N}{V} = \frac{\pi^2}{16} D^3 \frac{N}{V}.
\]  

The last term in Eq. (2.6) can be identified as the (dimensionless) second virial coefficient \( \tilde{B}_2 \) multiplied by the concentration \( c \). Note that \( c \tilde{B}_2 \) constitutes the excess part of the free energy which accounts for the interactions between the hard particles. Using Eq. (2.5), together with the isotropic value, \( \sigma \equiv 0 \), we obtain the following expression for the free energy in the isotropic phase

\[
\frac{\beta F_{\text{iso}}}{N} \sim \text{cst} + (\ln c - 1) + (1 - x) \ln(1 - x) + x \ln x
\] 

\[
+ c \left\{ 1 + \left( 2 + \frac{6}{\pi} \right) \left[ (1 - x) \frac{L_1}{D} + x \frac{L_2}{D} \right] \right\}.
\]  

(2.8)

In the nematic phase, matters are more complicated since the ODF is no longer a constant but a sharply peaked function. The excluded volume entropy is now given by

\[
\rho_j^{\text{nem}} = 4 \int \int |\sin \gamma| f_j(\theta) f_k(\theta') d\Omega d\Omega' \] 

\[
+ \frac{2}{\pi} \frac{L_j + L_k}{D} \int \int \left[ 3 - \frac{1}{2} \sin^2 \gamma + |\cos \gamma| \right] f_j(\theta) f_k(\theta') d\Omega d\Omega' + \mathcal{O}((L/D)^2).
\]  

(2.9)

Here, the following asymptotic expansion of the elliptic integral has been used [71]

\[
E(\sin \gamma) = \frac{\pi}{2} \left\{ 1 - \frac{1}{4} \sin^2 \gamma + \mathcal{O}(\sin^4 \gamma) \right\},
\]  

(2.10)

valid for small angles \( \gamma \). Note that this approximation is only justified for strongly aligned states where the ODF is a sharply peaked function. In the following we will use Gaussian trial ODFs with variational parameter \( \alpha_j \) to describe the angular distribution of the platelets \( j \) in the nematic state [34]

\[
f_j(\theta) \equiv \begin{cases} 
\frac{\alpha_j}{\pi} \exp[- \frac{1}{2} \alpha_j \theta^2] & \text{if } 0 \leq \theta \leq \frac{\pi}{2} \\
\frac{\alpha_j}{\pi} \exp[- \frac{1}{2} \alpha_j (\pi - \theta)^2] & \text{if } \frac{\pi}{2} \leq \theta \leq \pi
\end{cases}
\]  

(2.11)

An advantage of using these trial ODFs is that \( \sigma_j \) and \( \rho_{jk} \) become analytically tractable. Substituting Eq. (2.11) in Eq. (2.1) gives

\[
\sigma_j \sim \ln \alpha_j - 1, \quad j = 1, 2,
\]  

(2.12)

for the orientational entropy. For the excluded volume entropy in the nematic phase we will only retain the leading order terms of its asymptotic expansion for large \( \alpha_j \)

\[
\rho_{jk}^{\text{nem}} \sim \left[ \frac{8}{\pi} \left( \frac{1}{\alpha_j} + \frac{1}{\alpha_k} \right) + \frac{8}{\pi} \frac{L_j + L_k}{D} \left[ 1 + \mathcal{O}(\alpha_j^{-1}, \alpha_k^{-1}) \right] \right].
\]  

(2.13)

Henceforth, we neglect the \( \mathcal{O}(\alpha^{-1}) \) contribution in the second term, which is justified for very large values of \( \alpha \). This is a crucial step in our analysis, since the \( \mathcal{O}(L/D) \)-term now becomes independent of \( \alpha_j \) and the shape of \( f_j(\theta) \). The orientation of the platelets
in the nematic phase is therefore solely determined by the diameter of the platelets, which is identical for both components. As the plate thickness does not enter into the free energy anywhere else than via the $\mathcal{O}(L/D)$-term in Eq. (2.13) we can simplify our calculations considerably by using a single variational parameter, $\alpha = \alpha_j = \alpha_k$, which holds for both components. The above expression then reduces to

$$\rho_{jk}^{\text{nem}} \sim \frac{4}{\sqrt{\pi \alpha}} + \frac{8}{\pi} \frac{L_j + L_k}{D}.$$ (2.14)

The thickness contribution to $\rho^{\text{nem}}$ is now simply the ratio of the excluded volume between two parallel platelets in the nematic phase, $\pi D^2 (L_j + L_k)$, and the excluded volume $v_{\text{excl,iso}}^0$ between two randomly oriented platelets with zero thickness in the isotropic phase. Note that this contribution remains constant up to order $\mathcal{O}(\gamma^2)$ as can easily be inferred from Eq. (2.9) by expanding the trigonometric functions in the integrand.

Inserting Eq. (2.12) and Eq. (2.14) into the Helmholtz free energy Eq. (2.6) and minimizing with respect to $\alpha$ leads to a simple $c^2$-dependence of the Gaussian variational parameter \cite{5}

$$\alpha = \frac{4c^2}{\pi},$$ (2.15)

independent of the mole fraction $x$. Substituting all expressions back into the free energy Eq. (2.6) yields a simple expression for the free energy in the nematic phase

$$\frac{\beta F_{\text{nem}}}{N} \sim \text{cst} + 3 \ln c + \frac{4}{\pi} + x \ln x + (1 - x) \ln(1 - x) + \frac{16}{\pi} c \left[ (1 - x) \frac{L_1}{D} + x \frac{L_2}{D} \right].$$ (2.16)

To locate phase transitions, we must know the osmotic pressure and chemical potential of both species. These are calculated as standard derivatives of the free energy. In the nematic phase we obtain for the osmotic pressure (in dimensionless notation)

$$\tilde{\Pi}_{\text{nem}} \equiv -\frac{1}{2} \beta v_{\text{excl,iso}}^0 \left( \frac{\partial F_{\text{nem}}}{\partial V} \right)_{N_1,N_2,T} \sim 3c_n + \frac{16}{\pi} c_n^2 \left[ (1 - x_n) \frac{L_1}{D} + x_n \frac{L_2}{D} \right],$$ (2.17)

where the subscripts $n$ refer to the concentration and composition of the nematic phase. The (dimensionless) chemical potentials follow from

$$\tilde{\mu}_{j,\text{nem}} \equiv \beta \left( \frac{\partial F_{\text{nem}}}{\partial N_j} \right)_{N_j,V,T}, \quad j = 1, 2.$$ (2.18)

Expressions for the isotropic phase can be obtained likewise from Eq. (2.8).

We can summarize our results so far by focusing on the excess free energy in the nematic phase. Judging from Eq. (2.6) we see that the last term ($cB_2$) is essentially given by a double mole fraction average of the following quantity

$$c \rho_{jk}^{\text{nem}} \sim 2 + \frac{8}{\pi} c \frac{L_j + L_k}{D},$$ (2.19)

which is easily obtained by combining Eq. (2.14) and Eq. (2.15). From this we conclude that the leading order excess free energy, i.e. for platelets with zero thickness, is simply a constant. The $\mathcal{O}(L/D)$-term gives rise to an additional contribution which is linear in $c$. As to the osmotic pressure Eq. (2.17), we see that this leads to a quadratic correction
term, implying that the pressure of a (dense) nematic state is influenced considerably by the plate thickness.

We are, in principle, ready to construct the phase diagram by equating the osmotic pressure and the chemical potentials of the isotropic and nematic phases. In the next section we show how we can make a quantitative upgrade of the original Onsager theory in order to make plausible comparisons with the experimental results possible. By means of Parsons’ approach we indirectly account for the effect of many-body interactions which play an important role in systems of platelike particles.

### 2.2.1. Parsons free energy

Implementing Parsons’ approach to (binary) mixtures can in principle be carried out in a number of ways. In this thesis we shall use the simplest approach, introduced by Camp and Allen [48], which consists of replacing the orientation-dependent prefactor in Eq. (1.42) by

\[
\langle\langle \tilde{v}^{\text{excl}} \rangle\rangle / \tilde{v}_0 = \tilde{v}^{\text{excl,iso}} \tilde{B}_2,
\]

\[
\tilde{v}_0 = (1-x)v_{0,1} + xv_{0,2},
\]

\[
\phi = (1-x)\phi_1 + x\phi_2,
\]

with \(\phi\) the total volume fraction of particles, related to the dimensionless concentration and composition via

\[
\phi(c, x) = \frac{4}{\pi c} \left[(1-x)\frac{L_1}{D} + x \frac{L_2}{D}\right].
\]

Recalculation of the osmotic pressure and chemical potentials for the isotropic phase is now straightforward, using the definitions Eq. (2.17) and Eq. (2.18). The resulting expressions however involve additional derivatives of \(\tilde{f}_{CS}\) (Eq. (1.40) with respect to \(c\) and \(x\), due to their relation with \(\phi\) via Eq. (2.21). For the nematic state, minimization of the free energy with respect to \(\alpha\) now yields

\[
\alpha \sim \frac{4}{\pi} c^2 \tilde{f}_{CS}^2(\phi).
\]

The Onsager-Parsons free energy (denoted by superscript \(P\)) for the nematic phase thus reads

\[
\frac{\beta F^P_{\text{nem}}}{N} \sim \text{cst} + 3 \ln c + \ln \frac{4}{\pi} + x \ln x + (1-x) \ln(1-x) + 2 \ln \tilde{f}_{CS}(\phi)
\]

\[+ \frac{16}{\pi} c \tilde{f}_{CS}(\phi) \left[(1-x)\frac{L_1}{D} + x \frac{L_2}{D}\right].
\]

(2.23)

where the additional \(\ln \tilde{f}\) contribution arises from the orientational entropy Eq. (2.12). To compare with Eq. (2.17) we explicitly give the Onsager-Parsons osmotic pressure of the nematic phase

\[
\tilde{\Pi}^P_{\text{nem}} \sim c_n + \left[2c_n + \frac{16}{\pi} c_n^2 \tilde{f}_{CS} \left\{(1-x_n)\frac{L_1}{D} + x_n \frac{L_2}{D}\right\}\right] \left[1 + c_n \frac{\partial \ln \tilde{f}_{CS}}{\partial c}\right].
\]

(2.24)
2. Density inversion in mixtures of thin and thick hard platelets

Table 2.1. Typical dimensions and aspect ratios of the thick and thin platelets used in the present calculations [72].

<table>
<thead>
<tr>
<th>$D$ (nm)</th>
<th>$L_1$ (nm)</th>
<th>$L_2$ (nm)</th>
<th>$D/L_1$</th>
<th>$D/L_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>20</td>
<td>45</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

Note that the linear contribution $3c_n$ is retained but the presence of $\tilde{f}$ and its derivatives leads to a more complicated $c$-dependence. Similar expressions for the chemical potentials can be obtained by straightforward derivation.

2.3. Isotropic-nematic phase coexistence: density inversion

We can now construct phase diagrams by imposing the standard conditions of equal pressure and chemical potentials in the two coexisting phases. However, we are still left with two important, yet unspecified parameters, namely the typical aspect ratio of the thin and thick platelets, $D/L_1$ and $D/L_2$ respectively. Since it is our primary aim to account for the experimentally observed features, we restrict ourselves to a single combination of aspect ratios, rather than scanning the entire parameter space. We have chosen a particular combination of dimensions for the platelets under consideration, shown in Table 2.1. These values should resemble the experimental system, studied by van der Kooij et al. [60], in a reasonable way. The corresponding phase diagram is depicted in Fig. 2.2. The diagram clearly reveals a considerable degree of fractionation between the coexisting phases. The thick platelets are expelled from the nematic phase and prefer the isotropic phase. Moreover, the strong increase of the equilibrium osmotic
2.3. Isotropic-nematic phase coexistence: density inversion

pressure as a function of mole fraction indicates an upward shift of the $I - N$ transition densities in a pure system at increasing plate thickness.

When we want to study the possibility of an $I - N$ density inversion, we should calculate the total mass density of the isotropic and the nematic phases. The mass density is linearly proportional to the effective core volume fraction of the platelets

$$\phi_{\text{core}} = \frac{4}{\pi} c \left[ \left( 1 - x \right) \frac{L_1}{D} v_{1\text{core}} \frac{v_1}{v_1} + x \frac{L_2}{D} v_{2\text{core}} \frac{v_2}{v_2} \right], \quad (2.25)$$

which is related to the fact that, experimentally, the colloidal platelets consist of a (dense) gibbsite $(Al(OH)_3)$ core surrounded by a grafted polymer layer. The density of the polymer layer is approximately the same as that of solvent in which the platelets are immersed, so that the layer does not contribute to the total plate density. However, the polymer layer does contribute to the mutual excluded volume between two platelets. The dimensions given in Table 2.1 therefore apply to the grafted gibbsite platelets. The thickness of the polymer layer has been estimated at 4 nm [60] and the ratio of the core volume $v_{\text{core}}$ to the total volume $v$ of the platelet can be calculated using the values from Table 2.1, giving $v_{1\text{core}}/v_1 \approx 0.55$ and $v_{2\text{core}}/v_2 \approx 0.75$.

Fig. 2.3 reveals that a density inversion indeed takes place during the $I - N$ phase separation. Remarkably, the area in which the isotropic and nematic phase densities are inverted appears to cover a major part of the phase diagram. Only when the overall mole fraction is close to zero or one, i.e. in case of an almost pure system of either thin or thick platelets, fractionation is apparently not strong enough to accomplish a density inversion. In these situations, an isotropic upper phase will be found as in the regular cases. Equal phase densities are found at coexisting mole fractions $(x_i, x_n) = (0.13, 0.03)$ and $(0.96, 0.79)$, corresponding to $\bar{\Pi} = 36.7$ and 82.7, respectively.

We can also represent the phase diagram by plotting the core volume fraction versus the concentration, as shown in Fig. 2.4. Recall that the core volume fraction is directly
proportional to the mass density of the phases. In this phase diagram, we can draw dilution lines, i.e. straight lines radiating from the origin, along which the overall composition $x$ of the parent system remains constant. This representation clearly shows that the total plate number density in the nematic phase is always higher than that in the isotropic phase, irrespective of mole fraction (i.e. the slope of the dilution line). The density inversion therefore cannot be caused by an inversion of coexistence densities and hence must be driven solely by fractionation effects.

The slope of the tie lines are directly related to the density of the coexisting isotropic and nematic phases, i.e. a positive slope indicates a regular state (isotropic top and nematic bottom phase) whereas a negative one corresponds to an inverted state. The evolution of the tie lines give the impression of a “spiral staircase” with slope signs changing gradually from positive, to negative and back to positive upon increasing mole fractions. Finally, we remark from Fig. 2.4 that there is a distinct widening of the biphasic gap. The widening of the $I - N$ coexistence region is a generally established feature for bidisperse (and polydisperse) mixtures of anisometric particles, both in experiment [73–75] and theory [5,34,65] as will become clear in the rest of this thesis.

### 2.4. Nematic-Nematic Phase Coexistence

As mentioned earlier in this Chapter, the thickness of the platelets has a considerable influence on the osmotic pressure of a nematic phase at high concentrations (see Eq. (2.17). One may ask whether this can cause the nematic phase of a binary mixture of thin and thick platelets to demix into two nematic phases at sufficiently high concentrations.
2.4. Nematic-nematic phase coexistence

Figure 2.5. (a) Phase diagram in the $\bar{\Pi} - x$ plane of a binary mixture of thin platelets, $D/L_1 = 13$, and thick platelets, $D/L_2 = 4$, $(L_2/L_1 = 3.25)$. The nematic-nematic coexisting region is bounded by a lower critical point (cp). (b) As (a), for $D/L_1 = 15$ and $D/L_2 = 4$, $(L_2/L_1 = 3.75)$. Full curves denote stable phase boundaries, while the dotted curve represents a metastable one. The $I - N_I - N_{II}$ triple point is indicated by □.

In this section we study the relation between the thickness bidispersity, quantified by the thickness ratio $L_2/L_1$, and the topology of the phase diagram, in particular the existence of a nematic-nematic coexistence region. The occurrence of a demixing transition at a particular osmotic pressure can easily be identified by the presence of an instability region (or van der Waals-loop) in the chemical potential curve (plotted versus the mole fraction), for which $\partial \mu_j / \partial x_j < 0$.

In case of a nematic-nematic coexistence, there must be two states, denoted by $N_I$ and $N_{II}$, with different $c_n$ and/or $x_n$, having the same osmotic pressure and chemical potentials. We have investigated this possibility for mixtures with a fixed aspect ratio $D/L_2 = 4$ for the thick species. This means that we increase the degree of bidispersity by making the thin platelets thinner while keeping the thickness of the thick platelets fixed. In Fig. 2.5, the resulting phase diagrams are depicted for two different values of $D/L_1$.

A remarkable result is that the nematic-nematic transition is always present, irrespective of the thickness ratio $L_2/L_1 (> 1)$. Even near monodisperse systems (with $L_2/L_1$ close to 1) exhibit a nematic-nematic demixing transition, albeit at very high osmotic pressures. In our experimentally considered system $(D/L_1 = 9, D/L_2 = 4)$ we locate a nematic-nematic critical point at a coexistence pressure $\bar{\Pi} = 208$. Note that the nematic phases are probably metastable with respect to inhomogeneous liquid crystalline phases (e.g., smectic, columnar etc.) at these pressures. Obviously, increasing the thickness ratio stabilized the demixing transition in terms of a decrease of the critical pressure. At $L_2/L_1 \approx 3.3$, the $N - N$ binodals overlap with the $I - N$ coexistence region which gives rise to a triple coexistence between two nematic phases ($N_I$ and $N_{II}$) and an isotropic phase $I$ (Fig. 2.5(b)).
Let us now elaborate on the nematic-nematic demixing transition by trying to gain more insight in the underlying mechanism. A convenient way to study the mechanism behind a demixing transition is to construct the Gibbs free energy and investigate the behaviour of its individual entropic contributions. For the sake of simplicity, we will use the Onsager free energy Eq. (2.16) here, rather than the elaborate expressions obtained via Parsons rescaling. The Gibbs free energy (in units $k_B T$ per particle) is given by

$$g(\hat{\Pi}, x) \equiv \frac{\beta F}{N} + \hat{\Pi} e^{-1}(\hat{\Pi}, x).$$

(2.26)

The concentration $c(\hat{\Pi}, x)$ is obtained by inverting the osmotic pressure in the nematic state Eq. (2.17), which is simply quadratic in $c$. The individual entropic contributions are given by

$$g_{\text{mix}} \sim (1 - x) \ln(1 - x) + x \ln x,$$  

(2.27)

$$g_{\text{or}} \sim 2 \ln c(\hat{\Pi}, x) + \ln \frac{4}{\pi} + 1,$$  

(2.28)

$$g_{\text{ex}} \sim 2 + \frac{32}{\pi} c(\hat{\Pi}, x) \left[ (1 - x) \frac{L_1}{D} + x \frac{L_2}{D} \right],$$  

(2.29)

where the subscripts refer to the mixing, orientational and excluded-volume entropies, respectively. The subscripts for the nematic phase are left out for notational convenience. The ideal (translational) entropy is omitted here, since it has the same $c$-dependence as the orientational part.

It is advantageous to rescale the Gibbs free energy by subtracting the chemical potentials of the pure components, weighed by their mole fractions

$$g'(\hat{\Pi}, x) \equiv g(\hat{\Pi}, x) - \left[ (1 - x) \mu_1^0(\hat{\Pi}) + x \mu_2^0(\hat{\Pi}) \right].$$

(2.30)

Obviously, the same rescaling procedure can be applied to the individual entropic contributions. The motivation behind the rescaling of $g$ is to uncover the concave/convex curvature of the free energy by subtracting the dominant linear trend. Fig. 2.6 clearly shows that the demixing transition originates from a competition between mixing entropy and orientational entropy on the one hand (all favouring the mixed state) and excluded volume entropy on the other hand (favouring demixing). At sufficiently high osmotic pressures, the latter contribution becomes dominant and demixing occurs.

2.5. DISCUSSION

Our calculations based on the Gaussian approximation provide us with a fairly simple interpretation of the isotropic-nematic density inversion, as observed in experimental systems of polydisperse gibbsite platelets. It appears that this phenomenon indeed originates from a pronounced fractionation with respect to thickness between the isotropic and the nematic phase, as already suggested by van der Kooij et al. [60]. An isotropic-nematic density inversion can only be accomplished when the fractionation is strong enough to overrule the difference between the coexistence number densities of the isotropic and the nematic phase, for which $c_i < c_n$, irrespective of the overall composition.
2.5. Discussion

Figure 2.6. Rescaled Gibbs free energy $g'_{\text{tot}}$ of the nematic phase (in units $k_B T$ per particle) versus mole fraction $x$ of a binary mixture of thin platelets, $D/L_1 = 13$, and thick platelets, $D/L_2 = 4$, ($L_2/L_1 = 3.25$), at coexistence pressure $\bar{\Pi} = 140$ (dotted curve). The solid curves depict the contributions from the individual entropies; excluded volume ($g'_{\text{ex}}$), orientation ($g'_{\text{or}}$) and mixing ($g'_{\text{mix}}$). The local minima in $g'_{\text{tot}}$ indicate a demixing transition.

In this respect, we would like to stress the importance of the Parsons’ approach. The possibility of a density inversion strongly depends on the difference between the isotropic and nematic coexistence densities, i.e. the width of the coexistence region. It is a known feature that the Onsager theory overestimates both the coexistence densities and the width of the coexistence region. The theory predicts a strong first order transition ($\Delta (ND^3/V) > 1$) whereas Monte Carlo simulations only show a weak density jump [18]. It turns out that Parsons’ approach constitutes a significant quantitative improvement over the original Onsager theory since it both lowers the coexistence densities and narrows the density gap. It is therefore not surprising that our preliminary calculations solely based on the Onsager theory, could not establish a density inversion at any point in the phase diagram; the density jump was simply too large to be overruled by fractionation and hence an $I - N$ density inversion was not possible.

As pointed out earlier in this Chapter, we intend to compare our results with the experimental observations obtained by van der Kooij [60]. For this purpose, we have drawn a particular dilution line in Fig. 2.4 which resembles the experimental observations in a reasonable way. The “experimental” dilution line corresponds to a mole fraction $x = 0.07$. If a dilute system is concentrated along this dilution line, phase separation starts to occur at an overall volume fraction $\phi = 0.305$. The slope of the initial tie line is positive, indicating that an isotropic upper phase is formed initially. At $\phi = 0.32$ the dilution line and the equal density tie line intersect, indicating that both phases are equally dense at that point. At higher volume fractions, the slope of the tie lines becomes negative, indicating that the densities of the phases are inverted and a nematic upper phase will be formed. At $\phi = 0.351$ the system is fully nematic. The experimental phase boundaries are found to be somewhat lower ($\phi = 0.18$ and
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\( \phi = 0.30 \) [60]. Equal phase densities are found at a volume fraction of approximately 0.24 (Fig. 2.1(b)). We finally discuss a peculiar observation in relation with the aforementioned dilution experiments. Van der Kooij performed an additional fractionation experiment in which a suspension was brought to a volume fraction \( \phi = 0.29 \) close to the nematic phase boundary (\( \phi = 0.30 \)) and left to phase separate. The nematic upper phase was separated from the isotropic bottom phase and subsequently diluted. A remarkable observation was that this system did not exhibit a density inversion at any point in the isotropic-nematic coexistence region. This striking observation however cannot be explained by the present model. Fig. 2.4 shows that any dilution line close to the experimental dilution line must cross the horizontal tie line denoting equal phase densities. This means that, according to our phase diagram, splitting off the nematic phase from a system close to the nematic phase boundary should always give rise to a density inversion after dilution. We believe that this particular experimental observation is a clear manifestation of the polydisperse nature of a colloidal system of gibbsite platelets. This means that the system essentially comprises infinitely many platelike species with a continuous variation in thickness (and diameter), rather than a finite number of distinct species. Although the present binary model captures most of the experimental features it remains a serious simplification of a real colloidal system. In Chapter 7 we extend the binary model to a polydisperse one and show that this allows us to qualitatively account for the observations of the dilution experiment.

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