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# Entropic segregation in smectic phases of hard-body mixtures

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Received 14 January 2004

Published 30 April 2004

Online at [stacks.iop.org/JPhysCM/16/S2003](http://stacks.iop.org/JPhysCM/16/S2003)

DOI: 10.1088/0953-8984/16/19/012

## Abstract

Using an extension of the Parsons–Lee density-functional theory, we have calculated the phase behaviour of mixtures of hard bodies, focusing on the formation of smectic phases. The interactions are represented by hard spherocylinders, and the mixtures have two components of lengths  $L_1$ ,  $L_2$  and widths  $D_1$ ,  $D_2$ , respectively, with  $D_1 = D_2$ . The special case where one of the components is a hard sphere ( $L_1 = 0$ ,  $L_2 \neq 0$ ) is also studied. Particular emphasis is put on the interplay between smectic-phase formation and smectic–smectic segregation. In general, smectic–smectic segregation is seen to occur in a wide range of compositions and pressures, except when the length ratio  $q \equiv L_1/L_2$  is relatively close to unity, i.e. particles have similar lengths; in this case segregation appears only at high pressure. Finally, in the case where  $q$  is very different from unity and the composition is such that there is a small fraction of long molecules, even when the mixture is macroscopically homogeneous, there appears a microsegregated phase where the minority component is expelled to the interstitial regions between the smectic layers.

## 1. Introduction

Since the last decade there has been an increasing interest in the phase behaviour of colloidal liquid crystals. Here we will focus on a particular type of colloidal liquid crystal, namely a fluid made up of particles with size in the range 1 nm–1  $\mu$ m immersed in a molecular or atomic fluid that are sufficiently anisotropic in shape to form liquid-crystalline phases similar to those formed by many organic molecules. Also of interest are fluids formed by colloidal particles in a host that itself may be a liquid crystal, typically a nematic fluid. In this latter case interesting interaction effects between the colloidal particles can be mediated by the host fluid. This latter system will not be considered in this work.

Of particular interest are those colloidal liquid crystal mixtures formed by two components that, when already in pure form, are capable of exhibiting liquid-crystalline phases. In their pioneering work, Buining and Lekkerkerker [1] synthesized colloidal particles with anisotropic shapes and conducted experimental verification of the predictions of computer simulation that hard-core anisotropic particles exhibit a great variety of liquid crystal phases. They also analysed the phase behaviour of mixtures of such colloidal particles, and showed that there were interesting segregation effects interacting with liquid-crystal phase formation. These findings were confirmed theoretically using the Onsager theory [2]. In particular, it was shown that isotropic–isotropic segregation could be obtained for mixtures of hard spherocylinders (HSPCs) of the same diameters. In further work [3–8] other groups have generalized the type of mixtures, and nematic–nematic segregation has also been found.

Thus far very few studies have focused on the smectic phases that can result in these systems. HSPCs are the type of interactions mostly considered in previous work on nematic formation. But this model is known to exhibit smectic phases. It is then natural to ask ourselves whether mixtures of anisotropic colloidal particles may in general show smectic phases in the phase diagram, and if so what is the structure of these phases, i.e. the arrangement of the particles to form smectic layers. The theoretical analysis of this problem has only been partly undertaken so far. General considerations [9] indicate that the smectic order in mixtures of hard rods will appear at higher pressures than in one-component systems since particles of different lengths do not easily pack together to form well-defined layers. Stroobants [10] performed Monte Carlo simulations to investigate columnar versus smectic order in mixtures of parallel HSPCs of small length-to-width ratio and the same width, showing that the columnar phase may preempt smectic formation. Koda and Kimura [11] used the Onsager theory to make a stability analysis of the nematic phase of mixtures of parallel hard cylinders against smectic fluctuations. The particles were taken to have the same width but different lengths. Two types of smectic phase were found, one in which the layers are identical and contain a mixture of both types of particles, and another in which layers with different composition alternate. More recently, Koda *et al* [12] and Dogic *et al* [13] considered mixtures of HSPCs and hard spheres (HSs)—the latter can be considered as an HSPC where the length of the cylinder is zero. These studies were aimed at investigating the effect of adding spheres to a fluid of spherocylinders; the main findings are that there is a strong segregation between spherocylinders and spheres, and that sometimes the addition of a small number of spheres may stabilize the smectic phase of HSPCs, in what can be considered to be associated to a depletion mechanism. Segregation is associated with the formation of a microphase where two-dimensional layers of spherocylinders and spheres appear alternated. Finally, van Roij and Mulder [14] have studied a mixture of parallel cylinders using Onsager theory and a bifurcation analysis. They analysed the conditions under which the nematic–nematic segregation spinodal preempts the nematic–smectic and nematic–columnar spinodals, which occurs if the length ratio is more extreme than 1:5.

All these studies have considered parallel HSPCs. Therefore, a number of important questions remain regarding the effect of orientational order, the possible smectic structures that a mixture can form, and the validity of the Onsager theory in the treatment of smectic phases of mixtures of finite-length hard rods. In addition, all studies so far have been based on stability analyses and bifurcation theory, and therefore the real topology of the phase diagram and the true location of the binodal or coexistence lines associated with the phase transitions have not been analysed.

In this paper we have investigated theoretically the phase behaviour of a number of mixtures of HSPCs, using an extension of the classical Parsons–Lee (PL) theory. The theory has been suitably modified so as to include the possibility of the formation of layered phases. Also, in

contrast to previous work, full orientational freedom is assumed for the particles, which allows us to analyse the stability of different particle arrangements in the smectic layers, including the possibility that particles may lie in the interstitials between the layers with perpendicular orientation. The theory has been applied to binary mixtures of particles with different lengths but the same width. As a special case, we also consider mixtures where one of the two components is a HS. The results confirm previous findings for this latter system and, for general HSPC mixtures, indicate a rich phase behaviour with smectic phases of different structures. For mixtures with a large length ratio, the general behaviour involves a strong tendency for the two components to segregate into two distinct smectic phases, meaning that HSPCs of different lengths do not easily mix together to form a smectic structure. In this case, the smectic phases that have been found to be stable contain a small amount of one of the components, whose particles may tend to arrange in the interstitials between the layers formed by the other component depending on whether or not the minority component corresponds to the longer particles. This indicates that short particles in a smectic structure do not support long particles with centres of mass located right in the layers, presumably because this configuration destroys the smectic order, and microsegregated smectic phases are formed. The opposite situation, with a small number of short particles in a smectic structure of long molecules, leads to a standard smectic phase of identical layers with the same particle composition. Microsegregated smectic phases with transverse particles in the interstitial regions between the layers have always been observed to be metastable. As expected, mixtures with not so large length ratios also exhibit the standard smectic phase. However, at high pressure there also appears smectic–smectic segregation bounded by a lower critical point.

The paper is arranged as follows. In the next section we briefly introduce the model and provide some technical details on the numerical treatment. In section 3.1 we show some results pertaining to HSPC/HS mixtures, whereas in section 3.2 more general HSPC/HSPC mixtures are considered. We end with a summary of our work and with some conclusions, which are presented in section 4.

## 2. Theory and some computational details

### 2.1. Density-functional theory

We consider mixtures of general HSPCs, with lengths  $L_1, L_2$  and widths  $D_1, D_2$ , but restrict our calculations to the case  $D_1 = D_2$ . Our calculations are based on an extension of the PL theory modified to include smectic phases. The PL theory is an improved Onsager theory, originally intended to describe nematic order in otherwise pure, uniform liquids, i.e. the isotropic–nematic transition. Onsager theory is a virial expansion of the excess free energy of the liquid, truncated at second order in the density and, correspondingly, only includes correlations at the two-body level. Although formally exact in the limit where the length-to-width ratio of the particles tends to infinity and qualitatively correct in other cases, the results of the Onsager theory for the coexistence parameters for moderately shaped particles are generally poor. This defect was remedied in part by Parsons [15] and Lee [16], who devised a procedure to somehow resum the virial series approximately to all orders in the density. The resulting PL theory considerably improves on the results of the original Onsager theory. In the PL theory [16] the excess free energy  $\Delta F$  is written

$$\Delta F[f] = \Psi(\eta) \int \int d\hat{\Omega} d\hat{\Omega}' f(\hat{\Omega}) v_{\text{exc}}(\hat{\Omega}, \hat{\Omega}') f(\hat{\Omega}') \quad (1)$$

where  $f(\hat{\Omega})$  is the one-particle orientational distribution function, and  $v_{\text{exc}}(\hat{\Omega}, \hat{\Omega}')$  is the excluded volume associated with two particles oriented along the unit vectors  $\hat{\Omega}$  and  $\hat{\Omega}'$ .

The prefactor  $\Psi(\eta)$  depends on the packing fraction  $\eta = \rho_0 v$  of the fluid, with  $\rho_0$  the mean density and  $v$  the particle volume, and is the excess free energy corresponding to a fluid of HSs with the same packing fraction as the actual liquid-crystal system. The HS system is used as a reference system and, implicitly, the approximation inherent to the PL approach involves approximating the virial coefficients of order higher than the second in terms of those of a fluid of HSs.

The extension of the Onsager and PL theories to general mixtures is trivial. For two-component mixtures we have to consider two orientational distribution functions,  $f_1(\hat{\Omega})$  and  $f_2(\hat{\Omega})$ , and three different interactions, given by excluded-volume functions  $v_{\text{exc}}^{(ij)}(\hat{\Omega}, \hat{\Omega}')$ ,  $ij = 11, 12, 22$ , together with a suitable reference system onto which to map the spatial correlations. We define the composition of the mixture,  $x$ , to be the particle fraction for the first component,  $x = \rho_1^{(0)}/\rho_0$ , with  $\rho_0 = \rho_1^{(0)} + \rho_2^{(0)}$ , and  $\rho_1^{(0)}, \rho_2^{(0)}$  the mean densities of the components. The packing fraction of the mixture is  $\eta = \rho_1 v_1 + \rho_2 v_2 = \rho_0[x v_1 + (1-x)v_2]$ , with  $v_1$  and  $v_2$  the corresponding particle volumes. Then, as a first approximation, one can continue to use the same HS prefactor, which amounts to mapping the spatial correlations of the mixture onto those of an averaged HS fluid. The resulting excess free energy functional is

$$\Delta F[f_1, f_2] = \Psi(\eta) \int \int d\hat{\Omega} d\hat{\Omega}' \sum_{i=1}^2 \sum_{j=1}^2 \{x_i x_j f_i(\hat{\Omega}) v_{\text{exc}}^{(ij)}(\hat{\Omega}, \hat{\Omega}') f_j(\hat{\Omega}')\}. \quad (2)$$

The corresponding Onsager theory for the mixture would correspond to eliminating the density prefactor and substituting it by a factor 1/2. Note that the density prefactor simply affects the density range where the phase transitions appear, since the coupling between positions and orientations, given through the excluded volume terms, is identical in both theories. Various workers have used these approximations to study demixing transitions in hard-rod fluids. Lekkerkerker *et al* [17] used Onsager theory to investigate the isotropic–nematic transition, and found strong fractionation and reentrant phases in mixtures of hard rods of different lengths and equal diameters. Later, other workers have found isotropic–isotropic and nematic–nematic segregation in different mixtures [3–8] using Onsager theory.

However, both the Onsager and the PL theories do not explicitly include smectic phases, i.e. layered phases where the density distribution of centres of mass is inhomogeneous and show successive peaks separated by a distance of the order of the particle length. As a first step in this direction one has to consider the one-particle distribution function  $\rho(\mathbf{r}, \hat{\Omega})$ , and write a density-functional free energy in terms of this new variable, which takes account of the spatial correlations present in a smectic phase. For hard-core interactions the only presently available theory that includes these effects is that formulated by Somoza and Tarazona (ST) [18], which can be considered to be a sophisticated generalization of the PL approach. In this theory the excess free energy is written as

$$\Delta F[f] = \int d\mathbf{r} \left[ \frac{\Psi^{\text{PHE}}(\bar{\rho}(\mathbf{r}))}{\bar{\rho}_0^{\text{PHE}}(\mathbf{r})} \right] \int d\mathbf{r}' \int \int d\hat{\Omega} d\hat{\Omega}' \rho(\mathbf{r}, \hat{\Omega}) f_o(\mathbf{r} - \mathbf{r}', \hat{\Omega}, \hat{\Omega}') \rho(\mathbf{r}', \hat{\Omega}'). \quad (3)$$

Here  $\bar{\rho}(\mathbf{r})$  and  $\bar{\rho}_0(\mathbf{r})$  are averaged densities over a volume of the order of the volume of a properly chosen hard ellipsoid [19], and  $f_o$  is the overlap function of two HSs.  $\Psi^{\text{PHE}}$  is the excess free energy of a system of parallel hard ellipsoids. The latter system is used as a reference system, since its free energy can be obtained exactly in terms of that of a fluid of hard spheres through a trivial scaling transformation. The averaged densities are suitably weighted using a set of weight functions obtained from corresponding density-functional theories for HSs of the WDA type [20]. The above theory has been used successfully for HSs systems and other models and constitutes an ideal candidate for a study of mixtures. Nevertheless, this extension to mixtures is not completely direct since it is not immediately obvious how

**Table 1.** Comparison between coexistence data for the liquid-crystalline phase transitions in a system of pure hard spherocylinders with aspect ratio  $L/D = 5$ . PL: extended Parsons–Lee theory for smectics; MC: Monte Carlo data from [25]. Energy is in thermal energy units  $kT$ , and length is in units of the particle width  $D$ .

$L/D$	Theory	$P_{\text{IN}}$	$\rho_{\text{I}}$	$\rho_{\text{N}}$	$P_{\text{NS}}$	$\rho_{\text{N}}$	$\rho_{\text{S}}$
5.0	PL	1.236	0.090	0.095	1.620	0.105	0.109
	MC	1.117	0.089	0.089	1.438	0.102	0.108

the reference system should be chosen. Preliminary calculations with a simple version of the theory that uses an effective pure fluid of parallel hard ellipsoids did not provide physically sensible phases.

Faced with these problems, and before tackling the task of formulating a more complete theory of smectic phase in mixtures of hard-core fluids (either using a more elaborate ST approach or the more sophisticated fundamental-measure theory, still poorly developed for anisotropic hard bodies [21]), we have used a direct generalization of the PL theory to include the spatial structure. First, the one-particle distribution functions are written as  $\rho_i(\mathbf{r}, \hat{\Omega}) = \rho_i(\mathbf{r}) f_i(\mathbf{r}, \hat{\Omega})$ ,  $i = 1, 2$ , where  $\rho_i(\mathbf{r})$  are the number densities associated with the particle centres of mass, and the excess free-energy functional used is

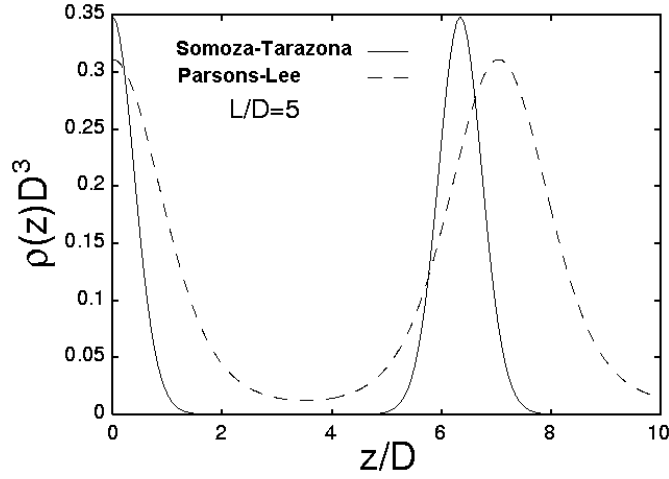
$$\Delta F[\rho_1, \rho_2] = \Psi(\eta) \int \int \int \int d\mathbf{r} d\mathbf{r}' d\hat{\Omega} d\hat{\Omega}' \sum_{i=1}^2 \sum_{j=1}^2 \times \{\rho_i(\mathbf{r}, \hat{\Omega}) f_o^{(ij)}(\mathbf{r} - \mathbf{r}'; \hat{\Omega}, \hat{\Omega}') \rho_j(\mathbf{r}' \hat{\Omega}')\}. \quad (4)$$

Here  $f_o^{(ij)}(\mathbf{r}; \hat{\Omega}, \hat{\Omega}')$  are the overlap functions of the three different interactions (unity if particles overlap and zero otherwise).

The above model, though certainly non-local, is not sufficiently non-local that, *a priori*, one could expect the highly correlated structure of a smectic phase to be accurately reproduced. However, the Onsager version (without the density prefactor) has been seen to reproduce a variety of aspects of the nematic–smectic transition in a pure HSPC fluid, albeit in a qualitative way—see, for example, [22–24]. The extended PL version provides nematic–smectic coexistence parameters with surprising accuracy (as is the case with the ST theory, the model reduces to the PL theory for a spatially uniform fluid so the coexistence parameters for the isotropic–nematic transition remain unaltered). Table 1 contains the coexistence densities and nematic order parameters for nematic and smectic phases for a one-component fluid of HSPCs with aspect ratio  $L/D = 5$ . Monte Carlo data extracted from [25] are included for comparison. The agreement is very reasonable even though, in principle, this value of the aspect ratio is relatively small for the PL theory to be accurate. Figure 1 shows the smectic density distributions from the extended PL theory and the ST theory for the smectic phase that coexists with the nematic. Although the smectic structure is softer, which can be understood in terms of the lack of non-local structure in the extended PL theory, the coexistence data are relatively well reproduced. It appears that the model qualitatively describes the smectic structure in the one-component fluid and reasonably describes the nematic–smectic transition. Therefore, it is expected that, with due caution, the results of the extended theory for mixtures can give at least qualitative trends as to what phase behaviour should be exhibited by these systems.

The final ingredient of the model is the ideal free energy, which is exactly given by

$$F_{\text{id}}[\rho_1, \rho_2] = kT \sum_{i=1}^2 \int \int d\mathbf{r} d\hat{\Omega} \rho_i(\mathbf{r}, \hat{\Omega}) [\log \rho_i(\mathbf{r}, \hat{\Omega}) - 1]. \quad (5)$$



**Figure 1.** Number density distribution for the coexisting smectic phase at the nematic–smectic phase transition for hard spherocylinders with length-to-width ratio  $L/D = 5$ . Continuous curve: ST theory. Dashed curve: extended PL theory.  $z$  is the coordinate along the director.

In terms of the local fractions  $x_1(\mathbf{r})$ ,  $x_2(\mathbf{r})$ ,

$$x_i(\mathbf{r}) = \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})}, \quad i = 1, 2, \quad x_1(\mathbf{r}) + x_2(\mathbf{r}) = 1 \quad (6)$$

and the total density distribution

$$\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r}) \quad (7)$$

the ideal free energy can be written as

$$F_{\text{id}}[\rho_1, \rho_2] = kT \int d\mathbf{r} \rho(\mathbf{r}) \left\{ \log \frac{\rho(\mathbf{r})}{4\pi} - 1 + \sum_{i=1}^2 x_i(\mathbf{r}) \log x_i(\mathbf{r}) + \sum_{i=1}^2 x_i(\mathbf{r}) \int d\hat{\Omega} f_i(\mathbf{r}, \hat{\Omega}) \log [4\pi f_i(\mathbf{r}, \hat{\Omega})] \right\}. \quad (8)$$

Inside the curly brackets we recognise the translational entropy, entropy of mixing, and rotational entropies, with a global minus sign.

## 2.2. Some approximations and computational details

Before we briefly describe the numerical implementation of the above density functional, we mention some simplifications and approximations used. First, since the system is layered along the direction imposed by the director (which we take along the  $\hat{z}$  direction), all distribution functions depend only on the coordinate  $z$ . Next, we have assumed that the orientational distribution functions do not depend on the  $z$  coordinate:  $f_i(z, \hat{\Omega}) = f_i(\hat{\Omega})$ . This approximation amounts to considering the nematic order parameter to be everywhere the same, i.e. that the spatial and orientational degrees of freedom are decoupled at the level of the one-particle distribution function. For a one-component smectic this approximation is exact in the limits of vanishing smectic order and complete smectic order, respectively. In between these limits the ST theory has shown that the approximation is very reasonable, and that it has

a negligible impact on the structure and thermodynamic properties of the smectic fluid [19]<sup>5</sup>. With these two simplifications, the excess free energy for the mixture is

$$\frac{\Delta F([\rho_1, \rho_2]; s_1, s_2)}{V} = \frac{\Psi(\eta)}{d} \int_0^d dz \sum_{i=1}^2 \sum_{j=1}^2 \rho_i(z) v_{\text{eff}}^{(ij)}(z - z'; s_1, s_2) \rho_j(z') \quad (9)$$

where  $V$  is the system volume,

$$v_{\text{eff}}^{(ij)}(z; s_i, s_j) \equiv \int \int d\hat{\Omega} d\hat{\Omega}' f_i(\hat{\Omega}) \left[ \int d\mathbf{R} f_o^{(ij)}(\mathbf{R}, z; \hat{\Omega}, \hat{\Omega}') \right] f_j(\hat{\Omega}') \quad (10)$$

are effective potentials, and  $\mathbf{R}$  are coordinates perpendicular to  $z$ , i.e.  $\mathbf{r} = (\mathbf{R}, z)$ .  $d$  is the smectic period. In (10) the kernel between squared brackets is calculated numerically. We have introduced (uniform) nematic order parameters  $s_i$  for each component. The orientational distribution functions are parameterized in terms of a single parameter  $\Lambda_i$ :

$$f_i(\hat{\Omega}; \Lambda_i) = \frac{e^{\Lambda_i P_2(\cos \theta)}}{\int d\hat{\Omega} e^{\Lambda_i P_2(\cos \theta)}} \quad (11)$$

where  $P_2(\cos \theta)$  is a Legendre polynomial, and  $\theta$  is the particle polar angle. The parameter  $\Lambda_i$  can be obtained from the nematic order parameter  $s_i$  through the definition of the latter by inversion of the function  $s_i(\Lambda_i)$ :

$$s_i(\Lambda_i) = \int d\hat{\Omega} f_i(\hat{\Omega}; \Lambda_i) P_2(\cos \theta). \quad (12)$$

Most of the calculations have been performed using the following approximation to evaluate the cross effective potential:

$$v_{\text{eff}}^{(12)}(z; s_1, s_2) \approx \bar{v}_{\text{eff}}^{(12)}(z, \bar{s}) \equiv \int d\hat{\Omega} d\hat{\Omega}' f_1(\hat{\Omega}; \bar{s}) \left[ \int d\mathbf{R} f_o^{(12)}(\mathbf{R}, z; \hat{\Omega}, \hat{\Omega}') \right] f_2(\hat{\Omega}'; \bar{s}) \quad (13)$$

which involves an averaged nematic order parameter  $\bar{s}$ ,

$$\bar{s} \equiv \frac{s_1 + s_2}{2}. \quad (14)$$

We have checked that, for phases where all particles point on average along the same direction, this approximation is numerically very accurate. Also, it is computationally very convenient, since it considerably reduces the numerical burden associated with the free-energy calculations. When searching for phases with transverse particles lying in the interstitial regions, this approximation is obviously not correct; in these cases we used the complete expression. For the other phases all calculations were done using the approximation.

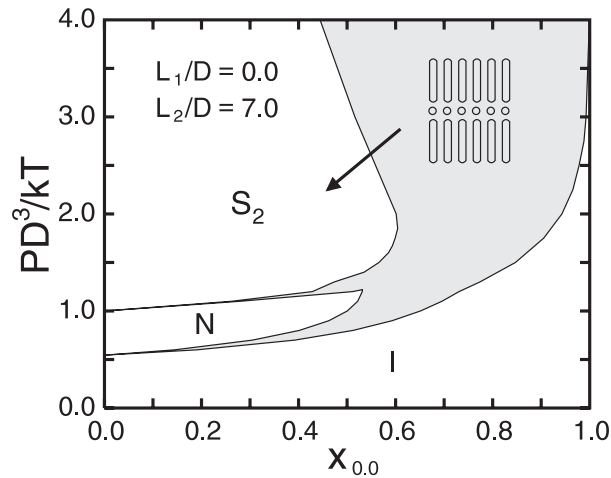
Finally, we need to specify a parameterization for the density distributions. A valid parameterization should reflect the structure of the lowest-order smectic structure that is to be expected in the mixture, which consists of alternating layers, each of them rich in one of the two components, which we will denote by  $S_2$ . A parameterization satisfying this criterion with a minimum set of parameters is

$$\rho_i(z) = \rho_i^{(0)} \frac{\exp(\lambda_i \cos(\frac{2\pi z}{d}))}{I_0(\lambda_i)} \quad (15)$$

where  $I_0(x)$  is the modified Bessel function of order 0 which ensures a proper normalization for the density distribution. For a  $S_2$  phase this parameterization assumes that each of the

<sup>5</sup> Use of the decoupling approximation changes the coexistence densities by less than 0.2% for  $L/D = 5$ . Note that this is not inconsistent with the finding by van Roij *et al* [24] that there is a strong modulation of the orientational distribution function of HPSC in the smectic phase; for a discussion see [19].





**Figure 2.** Pressure-composition phase diagram for a HSPC/HS mixture with spherocylinder length  $L_2 = 7D$  (the diameter of the spheres are the same as the width of the spherocylinders,  $D$ ). I (isotropic), N (nematic) and  $S_2$  phases are shown. The shaded regions indicate two-phase regions. The drawing shows the structure of the  $S_2$  phase schematically.

layers consists of a single component; the two components are out of phase, with different signs for the corresponding  $\lambda$ s. For a standard smectic, which will be denoted by S, the layers are identical and contain a varying composition depending on  $x$ . The  $\lambda$ s for the S phase have the same signs.

All calculations have been performed in the Gibbs ensemble by minimizing the Gibbs free energy  $G = F + PV$  with respect to the parameters

$$\rho_0, \lambda_1, \lambda_2, s_1, s_2, d \quad (16)$$

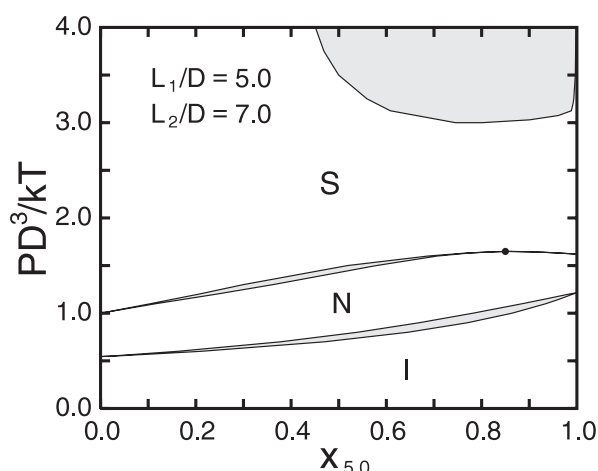
with pressure  $P$  and composition  $x$  kept fixed.

### 3. Results

In this section we present the results for different mixtures, always considering the case  $D_1 = D_2 = D$ . All the lengths in the results are given in units of  $D$ . Since we are mostly interested in smectic formation, mixtures have generally been chosen to be composed of particles with low length ratios in order to avoid nematic–nematic segregation [26]. We begin by considering the special mixtures consisting of HSPCs and HSs.

#### 3.1. Mixtures of HSPCs and HSs

In the case where one of the components consists of HSs, say  $L_1 = 0$ , the corresponding orientational distribution function is constant, and the nematic order parameter can be set to zero. The parameter space is therefore reduced by one parameter. Figure 2 shows the pressure ( $P$ )–composition ( $x$ ) phase diagram for the case  $L_2 = 7$ . Three phases are found: I (isotropic), N (nematic) and  $S_2$  (smectic). The latter consists of layers of HSPC particles alternating with layers of spheres (this phase has been called the *lamellar* microphase by Dogic *et al* [13] and was first predicted by Koda *et al* [12]). It is interesting to note the large amount of spheres that the smectic phase can support before phase separation (up to  $\sim 60\%$  in composition; naturally this corresponds to a low partial packing fraction of spheres, approximately 0.05). In [13] the stability of this phase is explained in terms of excluded volume arguments. It suffices to



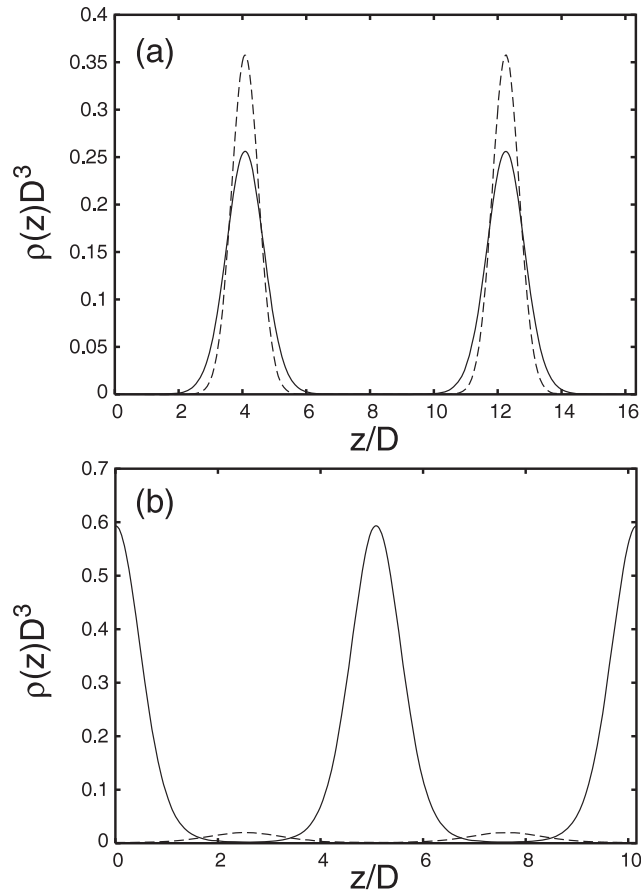
**Figure 3.** Pressure–composition phase diagram for a HSPC/HSPC mixture with lengths  $L_1 = 5D$  and  $L_2 = 7D$ . I (isotropic), N (nematic) and S (smectic) phases are shown. The shaded regions indicate two-phase regions.

say that the  $S_2$  phase seems to be the only stable smectic that can be formed in this mixture, since HSPC–HS interactions make the smectic arrangement into identical layers very unlikely with respect to arrangement into the  $S_2$  phase structure. The phase diagram features a triple point where N, I and  $S_2$  phases coexist. It also contains a small region of N stability; note that addition of spheres stabilizes the N phase with respect to the  $S_2$  phase. This latter phenomenon has been discussed in previous work for parallel hard rods. In [12, 13] Onsager theory was used to show that for sufficiently long particles addition of HSs can enhance the stability of the smectic phase, whereas below some critical ratio the effect is the opposite. The mixture that we have analysed is clearly below this critical ratio. Finally, we have observed that the smectic period increases with respect to the one-component smectic phase of the same total packing fraction when a small number of HSs is added to the fluid. This is not surprising since, as we have mentioned above, the HSs place themselves in the interstitial regions between the HSPC layers, pushing these layers apart.

### 3.2. Mixtures of HSPCs

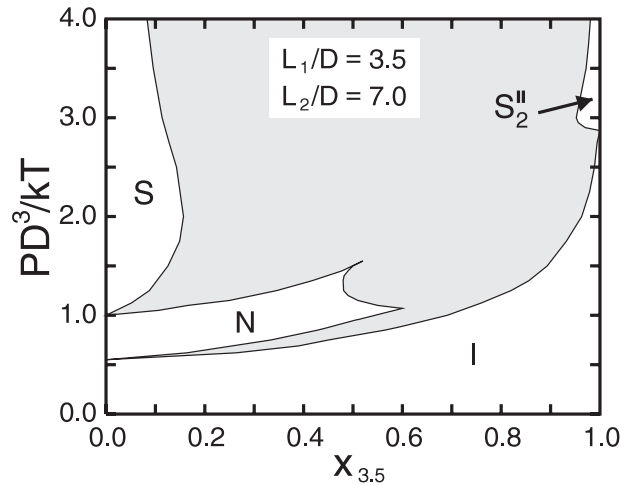
Figure 3 presents the  $P$ – $x$  phase diagram for the mixture  $L_1 = 5$ ,  $L_2 = 7$ , which has  $q = 0.71$ . Both species, when in pure form, have nematic phases and a region of nematic stability covers the whole composition range. This mixture consists of particles sufficiently similar in length that a standard smectic phase S also forms in the whole composition range. Figure 4(a) shows the density profiles of both species for a mixture with pressure  $PD^3/kT = 2$  and composition  $x_{5.0} = 0.5$ . The nematic–smectic transition shows an azeotropic point, indicated by a large full circle, where both phases have the same composition. At high pressure there appears a region of smectic–smectic segregation, bounded by a lower critical point. This highly asymmetric region is clearly displaced toward high values of composition, meaning that a smectic phase made by short particles does not easily accommodate long particles and tends to segregate into two phases: one with a similar concentration of both species, and the other almost exclusively composed of short particles.

The case  $L_1 = 3.5$ ,  $L_2 = 7$  ( $q = 0.5$ ) is shown in figure 5. In this case the mixture is more asymmetric and there is a dramatic change in phase behaviour with respect to the previous case. Since the first component does not have a nematic phase, the nematic region



**Figure 4.** Density profiles for the two species making up the mixture in the smectic phase. (a) Mixture with  $L_1 = 5D$ ,  $L_2 = 7D$  at pressure  $PD^3/kT = 2$  and composition  $x_{5,0} = 0.5$ ; continuous line: profile for component 1; dashed line: profile for component 2. (b) Mixture with  $L_1 = 3.5D$ ,  $L_2 = 7D$  at pressure  $PD^3/kT = 3$  and composition  $x_{3,5} = 0.95$ ; continuous line: profile for component 1; dashed line: profile for component 2.

does not reach the  $x = 1$  axis. The isotropic–nematic transition shows a typical loop structure at intermediate compositions. But the most interesting feature of the phase diagram is the strong fractionation shown by the smectic phase, which extends to relatively low pressures and even preempts the nematic phase. Smectic stability is constrained to small and large compositions, and in each case the structure of the smectic phase has a different nature. For low compositions the smectic phase is a standard S smectic, with a small amount of short particles mixed in the smectic layers formed by the long particles, which can support up to  $\sim 15\%$  of short particles. At high composition the smectic phase, denoted by  $S_2^{\parallel}$  in figure 5, shows a microsegregation phenomenon: long particles are expelled to the interstitial regions between the layers formed by the short particles. This process tends to make the cross excluded volume decrease, thereby increasing the entropy. Particles in the interstitials always point along the director; configurations with particles lying in transverse directions have never been observed to be thermodynamically stable. This statement is based on calculations performed using the full effective potential for the cross interaction, which depends separately on the two nematic order parameters. The approximation embodied in equation (13) is not appropriate when



**Figure 5.** Pressure–composition phase diagram for a HSPC/HSPC mixture with lengths  $L_1 = 3.5D$  and  $L_2 = 7D$ . I (isotropic), N (nematic), S (smectic) and  $S_2$  phases are shown. The shaded regions indicate two-phase regions.

searching for a  $S_2$  phase with transverse particle orientations in the interstitials, in which case  $s_1$  and  $s_2$  have different signs and the angle-averaged excluded area at a height  $z$ , equation (10), cannot be obtained using an average nematic order parameter. Figure 4(b) shows the density profiles of both species corresponding to a mixture at pressure  $PD^3/kT = 3$  and composition  $x_{3.5} = 0.95$ . In this case the mixture consists of only 5% of long particles, which are arranged out of phase with respect to the smectic layers formed by the particles of the other component.

An interesting question concerns the behaviour of the smectic period of the mixture with respect to the values adopted in the one-component smectics. In the case of the S phase the addition of a small amount of short particles makes the smectic period increase with respect to the one-component smectic phase of the same packing fraction. This effect may be related to an increase of the packing fraction in the layers, which is compensated by an increase in the smectic period. Note that this mechanism is different from that operating in the case of the HSPC/HS mixture, which may be related to the different smectic structure. For the  $S_2$  phase the smectic period of the mixture decreases with respect to the pure smectic. All these results are to be taken with due care, since they depend on a subtle free-energy balance that our simplified model may not be capturing properly. Therefore, checking these predictions against computer simulation would be interesting. Work along this avenue is in progress in our group.

#### 4. Discussion

In this work we have analysed the phase behaviour of different mixtures of HSPCs, putting emphasis on the smectic phases. When the length ratio  $q$  of the particles is sufficiently close to unity the system phase separates at high pressure into two smectic phases of different compositions but the same structure, which corresponds to standard smectic layers of the same composition. The smectic–smectic segregation transition is bounded by a lower critical point. In contrast, for length ratios quite different from unity, strong segregation in smectic phases is found. The system separates into two smectic phases of a different nature, with one of them exhibiting microsegregation. All these features are predicted using a theoretical model, an extended PL theory, that contains excluded-volume interactions exclusively.

Another point which deserves some comment is the possibility that the columnar phase can stabilize at the pressures where the smectic phase dominates the phase diagram according to the present theory. The work by Stroobants [10] indicates that polydispersity generally induces columnar order. However, this simulation work assumes parallel particles, while orientational disorder may penalise the columnar order with respect to the smectic order. Also, the range of compositions explored in [10] is around 0.5, while the smectic phases obtained in our work occur for low and high compositions. It is important to remember, in addition, that the one-component fluid of HSPCs with freely orienting particles does not show columnar stability. On the other hand, we may be certain that the solid phase will modify the high-pressure region of the phase diagram significantly. Although the crystal phases of the mixtures considered in this work have not been explored either by the present theoretical approach or by simulation, we believe that the smectic phases predicted here will not be preempted by the solid phase and, therefore, will be stable in some region of the phase diagram<sup>6</sup>. Naturally in order to elucidate this point further work will be needed.

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<sup>6</sup> For example, according to the simulations by Bolhuis and Frenkel on the HSPC fluid [25], the smectic phase of a pure HSPC fluid will crystallize at a reduced pressure  $PD^3/kT \approx 3.0$  (2.3) for aspect ratio  $L/D = 3.5$  (5). Our theory predicts transition pressures that are in quite good agreement with these simulation results. Therefore there are certainly regions of stability of the smectic phase on the  $x = 0$  and 1 axes of the phase diagrams for the mixtures considered in the present work, and it is natural to think that these regions will extend to mixtures of HSPC particles, at least when the compositions are not far from the one-component cases.