

Nematic-Smectic A and Nematic-Solid Transitions of Parallel Hard Spherocylinders from Density Functional Theory.

H. XU(*), H. N. W. LEKKERKERKER(*) and M. BAUS(**)

(*) *Van 't Hoff Laboratorium voor fysische en colloïdchemie
Rijksuniversiteit te Utrecht - Postbus 80.051, 3508 TB Utrecht, The Netherlands*

(**) *Faculté des Sciences, Université Libre de Bruxelles
CP 231, Campus Plaine, B-1050 Brussels, Belgium*

(received 28 June 1991; accepted in final form 26 September 1991)

PACS. 64.70 – Phase equilibria, phase transitions, and critical points.

PACS. 61.30B – Molecular theories of liquid crystals (inc. statistical mechanical theories).

PACS. 05.70F – Phase transitions: general aspects.

Abstract. – A simple density functional theory for the various liquid-crystalline phases of parallel hard spherocylinders is formulated on the basis of Pynn's ansatz for the direct correlation function of the spherocylinders. Fair agreement with the computer simulations is found.

It was Onsager [1] who showed for the first time that a nematic liquid crystalline phase can be formed, above a certain density, in a system of nonspherical molecules with purely repulsive (steric) interactions. Recent computer simulations [2] have confirmed this prediction and revealed moreover that the resulting phase diagram is very sensitive to the molecular shape and includes, for certain molecular aspect ratios, also smectic phases besides the isotropic, nematic and solid phases. At present, the simplest model system known [3] to exhibit a smectic phase consists of hard spherocylinders (*i.e.* cylinders of length L and diameter D capped at both ends with hemispheres of diameter D), which are constrained to remain parallel one to another. At low densities such a parallel hard spherocylinder (PHSC) system is always in a nematic (N) phase, while at high densities it forms a solid (S) phase with a (close packed) face-centred cubic (f.c.c.) structure. Moreover, above a critical value of the aspect ratio, L/D , a smectic A (SmA) phase forms for densities intermediate between those of the N and S phases. It is the purpose of this letter to study theoretically this competition between the N-S and N-SmA transitions of PHSC and to locate the N-SmA-S triple point in the density-aspect ratio plane.

A convenient theoretical framework for the study of phase transitions in systems of hard bodies is provided by the density functional theory of nonuniform fluids [4]. In this theory the (Helmholtz) free energy, F , of a system of N spherocylinders enclosed, at a temperature T ($\beta = 1/k_B T$), in a vessel of volume V is written as the sum, $F = F_{id} + F_{ex}$, of an ideal part

$$\beta F_{id}[\rho] = \int d\mathbf{x} \rho(\mathbf{x}) \{ \ln(\rho(\mathbf{x}) \Lambda^3) - 1 \} \quad (1)$$

and an excess part (due to the interactions)

$$\beta F_{\text{ex}}[\rho] = - \int d\mathbf{x} \int d\mathbf{x}' \rho(\mathbf{x}) \rho(\mathbf{x}') \int_0^1 d\lambda (1 - \lambda) c(\mathbf{x}, \mathbf{x}'; [\lambda\rho]) \quad (2)$$

both of which are viewed as functionals (indicated here by the square brackets) of the one-body density, $\rho(\mathbf{x})$, of the spherocylinders of centre \mathbf{r} and orientation \mathbf{u} , with \mathbf{u} being a unit vector along their symmetry axis and $\mathbf{x} = (\mathbf{r}, \mathbf{u})$. In (1), Λ denotes moreover the thermal wavelength while in (2) the direct correlation function (d.c.f.) of a system of density $\lambda\rho(\mathbf{x})$ has been written $c(\mathbf{x}, \mathbf{x}'; [\lambda\rho])$. For PHSC oriented along the z -axis ($\mathbf{1}_z$) we have $\rho(\mathbf{x}) = \rho(\mathbf{r}) \delta(\mathbf{u} - \mathbf{1}_z)$ for \mathbf{u} -variables normalized such that $\int d\mathbf{u} = 1$, and the \mathbf{u} -dependence in (1), (2) becomes thus trivial. The total free energy F will then be known once the distribution of the centres, $\rho(\mathbf{r})$, and the d.c.f., $c(\mathbf{r}, \mathbf{1}_z; \mathbf{r}', \mathbf{1}_z; [\rho])$, of the PHSC have been prescribed. Since $\rho(\mathbf{r})$ can always, as discussed further below, be expanded in terms of known functions and unknown order parameters (to be determined by minimizing F) the real problem clearly consists in the prescription of a realistic d.c.f. for the PHCS. For the ordered phases to be considered below no such information is as yet available and it is the basic assumption of the density functional theory of freezing [4] that for the evaluation of (2) this d.c.f. $c[\rho]$ can be replaced by the d.c.f. $c_0(\rho)$ of a spatially disordered fluid with an effective density $\bar{\rho}$:

$$c(\mathbf{r}, \mathbf{u}; \mathbf{r}', \mathbf{u}'; [\rho]) = c_0(\mathbf{r} - \mathbf{r}'; \mathbf{u}, \mathbf{u}'; \bar{\rho}[\rho]), \quad (3)$$

where the relation, $\bar{\rho} = \bar{\rho}[\rho]$, between the effective uniform density $\bar{\rho}$ and the original nonuniform density $\rho(\mathbf{r})$ has still to be determined as discussed further below. For nonspherical molecules, the determination of $c_0(\mathbf{r}; \mathbf{u}, \mathbf{u}'; \bar{\rho})$ is however itself already a nontrivial problem which is usually tackled [5] by numerically solving an integral equation such as the Percus-Yevick (PY) or the hypernetted-chain equation. Here, instead, we will use the analytic expression provided by the following ansatz, first suggested by Pynn [6], which relates the d.c.f. of a uniform fluid of (P)HSC to the PY d.c.f. of a fluid of hard spheres (HS) of diameter σ taken to be equal to the contact distance, $\sigma = \sigma(\mathbf{w}; \mathbf{u}, \mathbf{u}')$, of two HSC of orientations \mathbf{u} and \mathbf{u}' (later taken to be parallel to $\mathbf{1}_z$):

$$c_0(\mathbf{r}; \mathbf{u}, \mathbf{u}'; \bar{\rho}) = c_{\text{PY}}\left(\frac{|\mathbf{r}|}{\sigma(\mathbf{w}; \mathbf{u}, \mathbf{u}')} ; \bar{\rho}v_0\right), \quad (4)$$

where $w = \mathbf{r}/|\mathbf{r}|$ denotes the centre-to-centre direction at contact and $\eta = \bar{\rho}v_0$ the packing fraction for (P)HSC of volume v_0 and density $\bar{\rho}$. Pynn's ansatz (4) has the great advantage to lead to analytic expressions which in the limit of vanishing aspect ratio, $L/D \rightarrow 0$, where the HSC reduce to HS, provides a realistic (HS) d.c.f. It has been shown moreover that for hard dumbbells [7] the ansatz provided by (4) agrees surprisingly well with the numerical solutions of the PY equation. The approximation underlying (4) is most clearly exhibited by observing [8] that when (4) is used in (2) for a nematic phase it automatically leads to a decoupling of the angular and radial variables. At present, the only alternative to (4) or to the numerical solutions of integral equations [5] is provided by the use of weighted densities [9]. This however also involves considerable numerical work and here we prefer instead to investigate the consequences of the analytic expressions provided by (4). Our basic approximation rests thus on the use of (3), (4) in the exact equations (1), (2). In what follows we will describe the additional approximations required (for $\rho(\mathbf{r})$ and $\bar{\rho}[\rho]$) for the different phases (N, SmA, S) of the PHSC system together with the results obtained from the ensuing approximate density functional theory.

For the N-phase of the PHSC we have $\rho(\mathbf{r}) \equiv \rho$ and $\bar{\rho}[\rho] \equiv \rho$, since the centres are distributed uniformly with a density equal to ρ . Using these values in (1)-(4) immediately leads to the results that the thermodynamic data (free-energy, pressure and chemical potential) of the PHSC are given, within this approximation, by those of HS [10] of the same density (ρ) and volume (v_0) as the PHSC. This somewhat surprising result follows here because the total excluded volume of two PHSC is equal to $8v_0$, which is also the HS result. Because of this accidental degeneracy, the PHSC equation of state depends on the aspect ratio (L/D) only through the volume v_0 and reduces thus to a single curve when plotted in terms of the packing fraction ρv_0 (*e.g.*, fig. 1). An identical result was found in [5] for the numerical solutions of the PY equation for PHSC with $L/D > 1$ (but not for $L/D < 1$), whereas the computer simulations of [3] will reveal only a weak dependence of the equation of state on L/D . As can be seen from fig. 1, the present approximation is always quite satisfactory below a certain density, with the latter increasing with decreasing aspect ratio.

For the SmA phase the distribution of centres, $\rho(\mathbf{r})$, has a one-dimensional periodicity of period z_0 along the imposed z -direction: $\rho(\mathbf{r}) \equiv \rho(z) = \rho(z + z_0)$. In what follows it will be sufficient to locate the N-SmA transition. Since there are strong indications [3] that the latter is second order, we shall treat it as such here. We can thus perform a bifurcation analysis probing hereby the stability of the N-phase with respect to infinitesimal periodic density perturbations of the form

$$\rho(z) = \rho \left(1 + \varepsilon \cos 2\pi \frac{z}{z_0} \right), \tag{5}$$

where $0 < \varepsilon \ll 1$ and ρ is the average density of the SmA phase. Both the amplitude ε and the interlayer distance z_0 can be determined by minimizing the free energy (1), (2). Since ε is

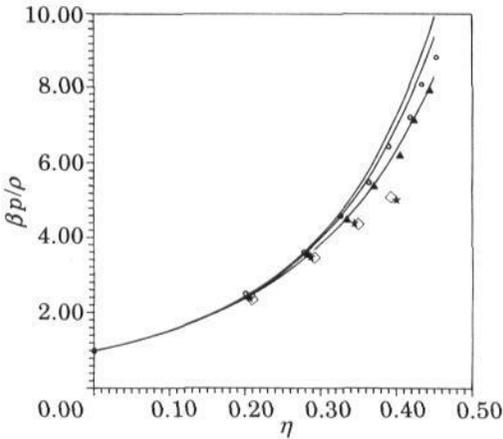


Fig. 1.

Fig. 1. – The compressibility factor, $\beta p/\rho$, of PHSC in the N-phase as a function of their packing fraction $\eta = \rho v_0$. The theoretical results obtained from Pynn's ansatz (4) correspond to the equation of state of HS of the same packing fraction as the PHSC. In solid lines we show the PY virial (lower curve), the Carnahan-Starling (middle curve) and the PY compressibility (upper curve) HS equations of state [10]. This should be compared to the simulation results of [3] for PHSC of $L/D = 0.25$ (circles), 0.5 (triangles), 3 (diamonds) and 5 (stars).

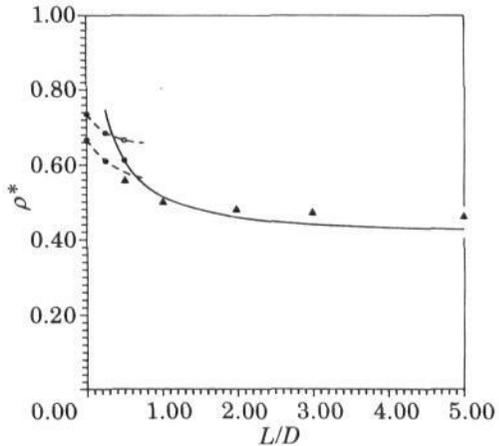


Fig. 2.

Fig. 2. – The reduced coexisting density, $\rho^* = \rho/\rho_{cp}$, vs. the aspect ratio, L/D , at the continuous N-SmA transition (solid line: from (6); triangles: from [3]) and the first-order N (lower curve)-S (upper curve) transition (dashed lines: from (9), (10); circles: from [3]).

TABLE I. – The reduced density, $\rho^* = \rho/\rho_{cp}$, and reduced pressure, $p^* = \beta p v_0$, at the continuous N-SmA transition of PHSC of aspect ratio, L/D , as obtained from (6) compared to the simulation results of [3].

L/D	Theory		Simulations	
	ρ^*	p^*	ρ^*	p^*
0.5	0.61	5.15	0.56	3.56
1	0.51	3.15	0.50	2.62
2	0.46	2.41	0.48	2.31
3	0.44	2.23	0.47	2.22
5	0.43	2.12	0.46	2.11

small we can still use $\bar{\rho}[\rho] = \rho$ in (3), (4) and expand (1), (2) around $\varepsilon = 0$, which corresponds to the N-phase free energy. This produces a Landau-type expansion for which the condition of marginal stability of the SmA phase reads then

$$\rho \int d\mathbf{r} \left\{ 2 \cos 2\pi \frac{z}{z_0} \right\} \int_0^1 d\lambda (1 - \lambda) c_{PY} \left(\frac{|\mathbf{r}|}{\sigma(\mathbf{w})}; \lambda \rho v_0 \right) = 1, \quad (6)$$

where $\sigma(\mathbf{w}) \equiv \sigma(\mathbf{w}; \mathbf{1}_z, \mathbf{1}_z)$. The bifurcation density, say $\rho = \rho_0$, for the onset of the N-SmA transition as obtained from (6) is shown in fig. 2. The agreement with the simulation results of [3] is fairly good, in particular a rapid increase of ρ_0 towards the close-packing density ρ_{cp} is obtained when the aspect ratio L/D is lowered towards the spherical limit ($L/D = 0$) where the transition has to disappear. Good agreement is found also for the interlayer distance z_0 and the pressure p at coexistence ($\rho = \rho_0$), with the quantitative agreement deteriorating slightly at the higher densities as a result of the loss in accuracy of the equation of state at these densities (see table I and fig. 3). We note that our results are qualitatively similar to those from earlier density functional treatments of the N-SmA transition of parallel hard particles [11].

Finally, we turn to the S-phase of the PHSC which has not yet been treated in the existing literature [5]. The distribution of the centres of the PHSC will now be parametrized

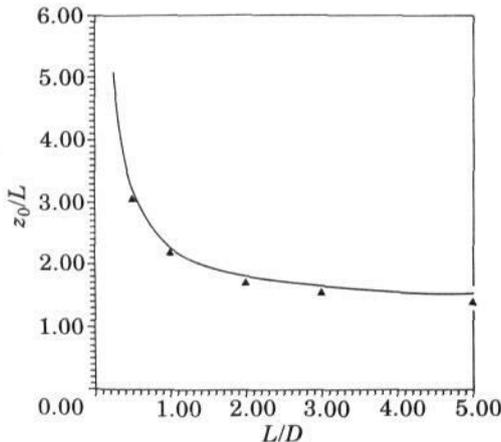


Fig. 3. – The reduced interlayer distance, z_0/L , of the SmA phase at the N-SmA coexistence vs. the aspect ratio L/D (solid line: from (6); triangles: from [3]).

in terms of Gaussian profiles [4] around the lattices sites $\{\mathbf{r}_i\}$:

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_i \exp[-\alpha(\mathbf{r} - \mathbf{r}_i)^2]. \quad (7)$$

The f.c.c. structure considered here can be formed by starting from a planar triangular lattice, with basis vectors of length a , followed by an ABC stacking of planes with an interplanar distance equal to $L + (2/3)^{1/2}a$. The order-parameter α of (7) will again be determined by minimizing the total free energy. To determine the effective density $\rho[\rho]$ of (3) for the PHSC described by (7) we will, in the spirit of (4), map the PHSC onto HS of the same volume by rescaling the densities with

$$\gamma \equiv \rho_{\text{cp}}^{\text{HS}} / \rho_{\text{cp}}^{\text{PHSC}},$$

the ratio of the close-packing densities of the two systems ($\gamma = (1 + 3/2L/D) / (1 + (3/2)^{1/2}L/D)$), or more explicitly

$$\bar{\rho}_{\text{PHSC}}[\rho] = \gamma^{-1} \bar{\rho}_{\text{HS}}[\gamma\rho], \quad (8)$$

where for $\bar{\rho}_{\text{HS}}[\rho]$ we will use the results of the GELA approximation [12] to which (7), (8) reduce in the spherical limit ($L/D \rightarrow 0$). For well-localized Gaussians ($\alpha D^2 \gg 1$) the ideal part (1) of the free energy per particle becomes now

$$\frac{\beta}{N} F_{\text{id}}[\rho] = \frac{3}{2} \ln(\alpha D^2 / \pi) - \frac{5}{2} + 3 \ln(L/D), \quad (9)$$

whereas, using (4) and (7), (8), the excess part (2) can be written as

$$\begin{aligned} \frac{\beta}{N} F_{\text{ex}}[\rho] = & - \sum_i \left(\frac{\alpha}{2\pi}\right)^{3/2} \int d\mathbf{w} \sigma^3(\mathbf{w}) \int_0^1 ds s^2 \exp\left[-\frac{\alpha}{2}(s\mathbf{w}\sigma(\mathbf{w}) - \mathbf{r}_i)^2\right] \\ & \cdot \int_0^1 d\lambda (1 - \lambda) c_{\text{PY}}(s; \gamma^{-1} \bar{\rho}_{\text{HS}}[\lambda\gamma\rho]), \end{aligned} \quad (10)$$

where the angular integral over \mathbf{w} has to be performed numerically. We have determined the N-S coexistence from (9), (10) as described in [12] for the small aspect ratios ($0 < L/D < 1$) for which (8) should remain a reasonable approximation. For the value $L/D = 0.25$ for which the simulations of [3] have found a first-order N-S transition we find $\rho_{\text{N}}/\rho_{\text{cp}} = 0.611$ and $\rho_{\text{S}}/\rho_{\text{cp}} = 0.687$ for the coexisting densities, in good agreement with the simulation results, respectively, 0.610 and 0.685. The reduced pressure, $\beta p v_0$, at coexistence which equals 4.75 for the simulations [3] is found here to be equal to 5.13 when the Carnahan-Starling equation of state is used to describe the HS thermodynamics. For the other values of the aspect ratio ($0 < L/D < 1$) the theoretical coexisting densities are shown in fig. 2. Notice that the coexisting densities first decrease with increasing L/D values, just like in the simulations, while for $0.4 < L/D < 0.7$ there is a competition between the N-S and the N-SmA transitions with the two transitions repelling each other leading to a minimum in the coexisting densities in the region of the N-SmA-S triple point. Needless to say, a more precise location of this triple point would require a better description of the N-SmA transition than the one provided by the bifurcation analysis performed above. This, together with the extension to freely rotating HSC [2], will be the subject of future work.

In conclusion, we found that the density functional theory of freezing [4, 12] together with Pynn's ansatz (4) for the d.c.f. leads to reasonable results for the phase diagram of PHSC.

* * *

This work is funded by the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) which is part of the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advanced Research). HX wishes to thank Dr. J. A. CUESTA for helpful discussions. MB acknowledges moreover the financial support of the Fonds National de la Recherche Scientifique.

REFERENCES

- [1] ONSAGER L., *Ann. Acad. Sci. (N.Y.)*, **51** (1949) 627.
- [2] FRENKEL D., LEKKERKERKER H. N. W. and STROOBANTS A., *Nature*, **332** (1988) 122; VEERMAN J. A. C. and FRENKEL D., *Phys. Rev. A*, **41** (1990) 3237.
- [3] STROOBANTS A., LEKKERKERKER H. N. W. and FRENKEL D., *Phys. Rev. A*, **36** (1987) 2923.
- [4] For recent reviews see, e.g., BAUS M., *J. Phys. Condensed Matter*, **2** (1990) 2111; OXTOBY D. W., *Nature*, **347** (1990) 725.
- [5] PERERA A. and PATEY G. N., *J. Chem. Phys.*, **89** (1988) 5861; CAILLOL J. M. and WEIS J. J., *J. Chem. Phys.*, **80** (1989) 7403.
- [6] PYNN R., *J. Chem. Phys.*, **60** (1974) 4579.
- [7] LADO F., *Mol. Phys.*, **54** (1985) 407.
- [8] COLOT J. L., WU X. G., XU H. and BAUS M., *Phys. Rev. A*, **38** (1988) 2022; CUESTA J. A., TEJERO C. F., XU H. and BAUS M., to be published.
- [9] SOMOZA A. M. and TARAZONA P., *J. Chem. Phys.*, **81** (1989) 517; PONIEWIERSKI A. and HOLYST R., *Phys. Rev. Lett.*, **61** (1988) 2461.
- [10] See, e.g., HANSEN J. P. and McDONALD I. R., *Theory of Simple Liquids* (Academic Press, London) 1976.
- [11] MULDER B., *Phys. Rev. A*, **35** (1987) 3095; SOMOZA A. M. and TARAZONA P., *Phys. Rev. Lett.*, **61** (1988) 2566; HOLYST R. and PONIEWIERSKI A., *Phys. Rev. A*, **39** (1989) 2742.
- [12] LUTSKO J. F. and BAUS M., *Phys. Rev. A*, **41** (1990) 6647.