

## High-density scaling solution to the Onsager model of lyotropic nematics

R. VAN ROIJ and B. MULDER

*FOM-Institute for Atomic and Molecular Physics (AMOLF)  
Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*

(received 3 January 1996; accepted 7 March 1996)

PACS. 61.30Cz – Theory and models of liquid crystals.

PACS. 61.30Gd – Orientational order of liquid crystals; electric and magnetic field effects on order.

PACS. 64.70Md – Transitions in liquid crystals.

**Abstract.** – We show that the exact orientation distribution function (ODF) of the Onsager model for the nematic liquid crystalline phase of thin hard rod-like particles at high density can be scaled onto a single curve, which needs to be determined numerically only once. The scaling solution is in better agreement with simulation results on a system of spherocylinders of length-to-width ratio  $L/D = 40$  than the Gaussian ODF, hitherto believed to be the best representation. The phase behaviour determined from the scaling solution, and from its first-order low-density correction, are compared to the exact results.

*Introduction.* – The study of the phase behaviour of rod-like particles dates at least back to the experimental work of Zocher [1], who discovered in the 1920's that a solution of rod-like particles undergoes a phase transition from an isotropic to an anisotropic liquid upon increasing the concentration. In the latter phase, usually referred to as the nematic liquid crystalline phase, the particles are preferentially oriented along a specific direction in space, called the director. The isotropic-to-nematic phase transition was successfully explained theoretically in terms of the interparticle interactions by Onsager [2] in the 1940's. Onsager showed that the short-range repulsion (modelled as a hard-core interaction) between rigid, infinitely long rods is sufficient to explain qualitatively the experimentally observed transition.

A key concept in Onsager's theory is the orientation distribution function (ODF), giving the fraction of particles with a specific orientation. For a given concentration of rods, the equilibrium ODF is the one that minimizes Onsager's free-energy expression. At low concentrations the ODF is orientation independent, describing the isotropic phase, while the ODF at higher concentrations is peaked about the director, characteristic for the nematic phase. The functional form of the nematic ODF in Onsager's theory is determined by a non-linear integral equation, resulting from the stationarity condition on the free energy with respect to variations in the ODF [3]-[6]. This density-dependent self-consistency equation has been solved numerically by various methods. One approach consists in the numerical determination

of the coefficients of the series expansion in Legendre polynomials of the ODF [4]. Another numerical approach consists in the calculation of the ODF discretized on a grid of orientations [6]. The advantage of both methods is that they do not impose the functional form of the ODF, if the number of basis functions is sufficiently large or the grid sufficiently fine. An important disadvantage is that a new calculation of the ODF is required for every new density considered. An alternative approach to determine (approximate) thermodynamic equilibrium ODFs is a variational method. This method is based on trial ODFs with variational parameters, which must be adjusted such as to minimize the free energy *in the subspace spanned by the trial form*. The main advantage of this method is that some trial ODFs (in practice only some of those with just one variational parameter) allow an analytic treatment of the “minimization” procedure. A clear disadvantage is that the trial ODF is not a solution of the exact stationarity condition, and therefore does not give rise to the exact minimum of the free-energy functional at the density considered. It turns out that the quality of the determination of the thermodynamic quantities depends sensitively on the choice of the trial ODFs. In the case of monodisperse hard rods, for instance, it is known that the prediction of the density of the nematic phase in coexistence with the isotropic phase is off by more than 20% if a Gaussian trial ODF is used [7]. However, it is generally assumed that the ODF at densities far above the ordering transition (when it is sharply peaked about the director) is well represented by a Gaussian. To our knowledge, this assumption has never been tested. In this letter we present an analysis of the functional form of peaked ODFs in the Onsager theory. The main result is that there exists a unique curve onto which all high-density ODFs can be mapped via a scaling relation.

We consider a system of hard rods of length  $L$  and diameter  $D$  with  $L \gg D$ . For these highly elongated rods the excluded volume of a pair of rods with orientations  $\hat{\omega}$  and  $\hat{\omega}'$  is given by  $2L^2D|\sin\gamma(\hat{\omega}, \hat{\omega}')|$ , where  $\gamma$  is the angle between their long axes [2]. Onsager showed that the free energy of this system (per particle per  $k_B T$ ) at a given number density  $n$  can be written as

$$f = \log c + \int d\hat{\omega} \psi(\hat{\omega}) \log \psi(\hat{\omega}) + \frac{4c}{\pi} \int d\hat{\omega} d\hat{\omega}' |\sin\gamma| \psi(\hat{\omega}) \psi(\hat{\omega}'), \quad (1)$$

where we denoted the ODF by  $\psi$  and the dimensionless density by  $c = (\pi/4)L^2 D n$ . At a given density  $c$ , this free energy is minimized by the equilibrium ODF, which we assume to have uniaxial symmetry, so that  $\psi(\hat{\omega}) = \psi(\theta)$ , where  $\theta$  denotes the polar angle of the rod orientation with respect to the nematic director. The first variation of eq. (1) with respect to ODFs of fixed unit norm leads to the non-linear self-consistency condition for the equilibrium ODF

$$\log \psi(\theta) + \frac{8c}{\pi} \int_0^\pi d\theta' \sin\theta' K(\theta, \theta') \psi(\theta') = \mu, \quad (2)$$

where the Lagrange multiplier  $\mu$  is used to fix the normalization and the azimuthally averaged kernel is given by

$$K(\theta, \theta') = \int_0^{2\pi} d\varphi |\sin\gamma| = \int_0^{2\pi} d\varphi \sqrt{1 - (\cos\theta \cos\theta' + \sin\theta \sin\theta' \cos\varphi)^2}. \quad (3)$$

It is easily checked that the isotropic ODF  $\psi_{\text{iso}} = 1/(4\pi)$  is a solution of eq. (2) for any  $c$ . The bifurcation analysis in [5] showed that this isotropic solution becomes absolutely unstable with respect to nematic perturbations for  $c \geq 4$ .

Here we first note that the Lagrange multiplier  $\mu$  in eq. (2) can be eliminated by introducing the reduced distribution

$$\phi(\theta) = \frac{\psi(\theta)}{\psi(\theta=0)}. \quad (4)$$

Next, we make use of the fact that the distribution is up-down symmetric so that  $\phi(\theta) = \phi(\pi - \theta)$ . These two facts allow us to rewrite eq. (2) as

$$\log \phi(\theta) + \frac{8c}{\pi} \frac{\int_0^{\pi/2} d\theta' \sin \theta' (K(\theta, \theta') - K(0, \theta')) \phi(\theta')}{2\pi \int_0^{\pi/2} d\theta' \sin \theta' \phi(\theta')} = 0. \quad (5)$$

Note that eq. (5) is still formally exact. Our analysis now proceeds from the observation that solutions  $\phi(\theta)$  of eq. (5) become increasingly peaked about  $\theta = 0$  as  $c$  increases. It is therefore natural to introduce a scaled angle  $t$  which measures the variations of the ODF on a scale corresponding to the actual width of the distribution at a given concentration. The correct choice turns out to be the simplest one, *i.e.*

$$t = c\theta, \quad (6)$$

where  $c$  is again the dimensionless density. This choice follows readily from the observation from eq. (3) that

$$cK\left(\frac{t}{c}, \frac{t'}{c}\right) = K_0(t, t') + \mathcal{O}\left(\frac{1}{c^2}\right), \quad (7)$$

where  $K_0$  can be calculated analytically in terms of the hypergeometric function  ${}_2F_1$

$$K_0(t, t') = 2\pi(t + t') {}_2F_1\left(-\frac{1}{2}, \frac{1}{2}; 1; \frac{4tt'}{(t + t')^2}\right). \quad (8)$$

Upon inserting eqs. (6) and (7) into (5), we observe that solutions  $\phi$  must satisfy the scaling relation

$$\phi\left(\frac{t}{c}\right) = \phi_0(t) + \mathcal{O}\left(\frac{1}{c^2}\right), \quad (9)$$

where the unique scaled ODF  $\phi_0$  is the solution of

$$\log \phi_0(t) + \frac{4}{\pi^2} \frac{\int_0^\infty dt' t' (K_0(t, t') - K_0(0, t')) \phi_0(t')}{\int_0^\infty dt' t' \phi_0(t')} = 0. \quad (10)$$

Note that eq. (10) is independent of  $c$  and needs to be determined numerically only once. We calculated  $\phi_0(t)$  with the iterative method of ref. [6] on an equally spaced grid of 300 points on the interval  $0 \leq t \leq 6$ , beyond which  $\phi_0$  is vanishingly small. This is a justification *a posteriori* of the substitution of the exact upper bound  $\pi c/2$  of the  $t$ -integrations in eq. (10) by  $\infty$ , which is harmless even down to the isotropic-nematic bifurcation density at  $c = 4$ .

From eqs. (4) and (9) we find that the ODF at a given (high) density  $c$  is given by  $\psi(\theta) = \psi_0(\theta) \times (1 + \mathcal{O}(1/c^2))$ , where the asymptotic ODF is given by

$$\psi_0(\theta) = \frac{c^2}{4\pi} \frac{\phi_0(c\theta)}{\int_0^\infty dt' t' \phi_0(t')} = \frac{c^2}{4\pi\Xi} \phi_0(c\theta) \quad (11)$$

with  $\Xi = 0.644434$ . We now compare  $\psi_0$  with the numerically exact ODF  $\psi_e$ , calculated for several densities with the numerical method of ref. [6]. We also make a comparison with the well-known Gaussian approximation  $\psi_G$ , where the ODF is assumed to have the form  $\psi_G(\theta) \propto \exp[-\alpha\theta^2/2]$ , with  $\alpha$  the variational parameter. Optimizing the free energy with respect to  $\alpha$  yields  $\alpha = 4c^2/\pi$ , as first discussed by Odijk [8]. Hence, one finds that  $\phi_G(\theta) = \psi_G(\theta)/\psi_G(0) = \exp[-(2/\pi)(c\theta)^2] = \exp[-(2/\pi)t^2]$ . This shows that the scaling of the *width* of the distribution implied by the Gaussian approximation is in fact correct, albeit

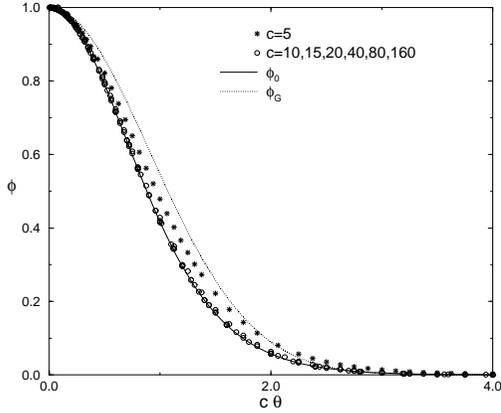


Fig. 1.

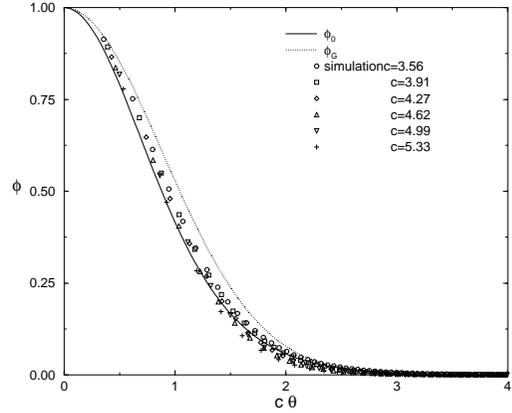


Fig. 2.

Fig. 1. – ODFs scaled to unity at  $c\theta = 0$  as a function of  $c\theta$ . The drawn curve is the asymptotic result  $\phi_0$ , the dotted curve is the Gaussian approximation  $\phi_G = \exp[-(2/\pi)(c\theta)^2]$  and the marks represent the numerically exact ODFs at several densities. We distinguished between the ODF at  $c = 5$  (denoted by  $*$ ) and  $c \geq 10$  (denoted by  $\circ$ ), to indicate that the asymptotic result is already very accurate for  $c \geq 10$ .

Fig. 2. – Scaled ODFs obtained from simulation of hard spherocylinders with  $L/D = 40$  at various densities, compared to the asymptotic  $\phi_0$  and Gaussian  $\phi_G$ .

that in this case one is in the scaling regime at *all* densities. The comparison made in fig. 1, however, shows that the *shape* of the distribution differs from the true asymptotic result. Indeed we see that the numerically exact curves for several values of  $c \geq 10$  (denoted by the  $\circ$  in fig. 1) are very well represented by the single asymptotic curve  $\phi_0(c\theta)$ . The asymptotic curve is of about the same accuracy as the dotted Gaussian curve in the case of  $c = 5$ , which corresponds to a density close to the isotropic-nematic transition. The asymptotic scaling ODF also appears to be a fair representation of the ODF even in the case of hard rods with a finite length-to-width ratio. In fig. 2 we show the comparison with results obtained on a simulation of hard spherocylinders of length-to-width ratio  $L/D = 40$ . The scaled ODFs obtained from the simulation for a variety of densities above the isotropic-nematic transition are seen to correlate well with the theoretical asymptotic form, and markedly less well with the Gaussian approximation.

The scaling ansatz equation (6) can also be shown to generate a full asymptotic expansion of the problem in powers of  $1/c^2$ . We have calculated the first correction to the asymptotic ODF, which involves the calculation of  $\phi_2(t)$ , defined by  $\phi(t/c) = \phi_0(t) + \phi_2(t)/c^2 + \mathcal{O}(1/c^4)$ . This calculation requires the second-order term of eq. (7), which can also be determined analytically. To illustrate the quality of this correction in the case of  $c = 5$ , we plot for this density the asymptotic, the lowest-order-corrected and the numerically exact reduced ODF in fig. 3. Clearly, the lowest-order correction provides a substantial improvement to the asymptotic result.

Our asymptotic approximations for the ODF also lead to approximations for the free energy and hence to predictions of the phase behaviour of the system. In fig. 4 we have plotted the predicted free energies for the nematic branches  $f_0$ ,  $f_2$ , obtained from our analysis,  $f_G$  from the Gaussian approximation and the exact  $f_e$ , numerically determined as in [6], as well as the trivial isotropic branch  $f_{\text{iso}}$ , all plotted as functions of  $1/c$  for convenience. In order to make the double-tangent construction more visible to the eye we have subtracted a (irrelevant)

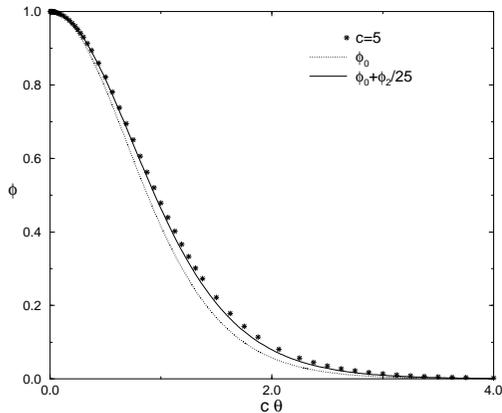


Fig. 3.

Fig. 3. – Comparison of the exact scaled ODF  $\phi$  at  $c = 5$  (denoted by  $*$ ) with the asymptotic result  $\phi_0$  (dotted curve) and the corrected result  $\phi_0 + \phi_2/c^2$ , where we set  $c = 5$ .

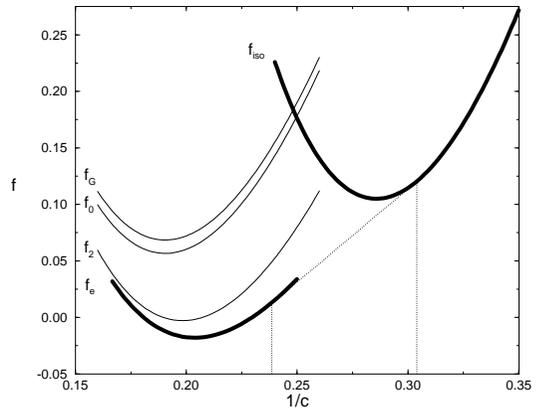


Fig. 4.

Fig. 4. – Helmholtz free energy of the isotropic and nematic phase as a function of  $1/c$ , which allows a common-tangent construction, represented by the dotted line, to determine the isotropic-nematic coexistence. From all curves we have subtracted the fit linear in  $1/c$  through  $f_e$ , the full numerically determined free energy of the nematic phase; this does not affect the common tangent construction.

common linear contribution in  $1/c$ . As expected,  $f_e$  is smaller than all approximations, which are based on non-exact ODFs. We also see that  $f_2$  is significantly more accurate than  $f_0$  and  $f_G$ , at least in the vicinity of the isotropic-nematic transition. At larger values of  $c$ , the curves  $f_0$ ,  $f_2$  and  $f_e$  will coalesce, while  $f_G$  remains separated from them by a (explicitly calculable) constant.

TABLE I. – *The predicted coexistence densities and the jump in the order parameter from the approximations  $f_G, f_0$  and  $f_2$  discussed in the text as compared to the exact results  $f_e$ .*

	$c_{\text{iso}}$	$c_{\text{nem}}$	$S_{\text{nem}}$
$f_G$	3.45	5.12	0.910
$f_0$	3.436	5.080	0.9059
$f_2$	3.338	4.598	0.8852
$f_e$	3.290	4.191	0.7922

The results obtained for the isotropic-nematic phase transition are summarized in table I. The table reveals that the Gaussian and the asymptotic result are approximately of the same, relatively low, accuracy in the density regime of the isotropic-nematic transition, while the  $\mathcal{O}(1/c^2)$  correction again provides a substantial improvement.

In summary, we have considered the functional form of ODFs in the nematic phase of hard-rod systems as described by Onsager's second virial theory. We have shown that the high-density ODFs can all be scaled onto one single curve, which represents the exact ODF for all densities  $c \geq 10$  very accurately. Once calculated, the scaling solution provides a convenient tool for the analysis of high-density behaviour of hard-rod systems. An application of this idea to the stability of mixtures with particles of different length will be published elsewhere.

\*\*\*

We are indebted to P. BOLHUIS for providing us with the simulation results on the hard spherocylinders and to Daan Frenkel for carefully reading the manuscript. This work is part of the research programme of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)”, which is financially supported by the “Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO)”.

## REFERENCES

- [1] ZOCHER H., *Z. Anorg. Chem.*, **147** (1925) 91.
- [2] ONSAGER L., *Ann. N.Y. Acad. Sci.*, **51** (1949) 627.
- [3] LAKATOS K., *J. Stat. Phys.*, **2** (1970) 121.
- [4] LASHER G., *J. Chem. Phys.*, **53** (1970) 4141.
- [5] KAYSER R. F. and RAVECHÉ H. J., *Phys. Rev. A*, **17** (1978) 2067.
- [6] HERZFELD J., BERGER A. E. and WINGATE J. W., *Macromolecules*, **17** (1984) 1718.
- [7] VROEGE G. J. and LEKKERKERKER H. N. W., *Rep. Prog. Phys.*, **55** (1992) 1241.
- [8] ODIJK T., *Macromolecules*, **19** (1986) 2313.