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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: W. L. Wagner (1997): Properties of an Ideal Nematic Gay-Berne Fluid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 33-38

To link to this article: http://dx.doi.org/10.1080/10587259708041970

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Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 33–38
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PROPERTIES OF AN IDEAL NEMATIC GAY-BERNE FLUID

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Abstract Structural and thermodynamic properties of the perfectly ordered Gay-Berne model are calculateded. Applying perturbation methods we try to establish a relation between the soft Gay-Berne potential and the hard-core potential of ellipsoids of revolution. The determination of the axial parameters of the ellipsoid is the main task and also influences the structural properties of our model.

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INTRODUCTION

The Gay-Berne interaction potential[1] is well suited for describing essential features of mesogenic phases of linear particles. We apply this interaction model for the case of perfect parallel orientation of the constituent particles. We calculate some structural as well as thermodynamic properties.

The idea of the paper goes as follows: The properties of a system of hard spheres are well known from the theory of simple liquids. In case of perfect orientational order hard spheres and hard ellipsoids of revolution are related by a simple mapping procedure[2]. Hard ellipsoids can be used to approximate a system of anisotropic particles interacting via soft repulsion in the frame work of the blip-function theory[4]. The Gay-Berne interaction can be reduced to a soft repulsive potential with the help of the WCA-separation[3].

THEORY

The Gay-Berne interaction potential takes the following simple form in case of perfect orientational order

$$u_p(r,\cos\theta) = \varepsilon(\theta)*[(r/\sigma_0-\sigma_p(\theta)+1)^{-12}-(r/\sigma_0-\sigma_p(\theta)+1)$$

$$\varepsilon(\theta) = 4\varepsilon_0/\sqrt{(1-\chi^2)}*(1-2*\chi'/(1+\chi')\cos^2\theta)^2 \qquad \text{strength parameter}$$

$$\sigma_p(\theta) = (1-2*\chi/(1+\chi)\cos^2\theta)^{-1/2} \qquad \text{angle-dependent shape factor}$$

$$\chi = (\sigma_2^2-\sigma_1^2)/(\sigma_2^2+\sigma_1^2)\,,\ \chi' = (\sqrt{(\varepsilon_s/\varepsilon_e)}-1)/(\sqrt{(\varepsilon_s/\varepsilon_e)}+1)\,.$$

σ_2/σ_1 represents the axial ratio of the Gay-Berne particles and $\varepsilon_s/\varepsilon_e$ is the corresponding ratio of the well depths and θ is the angle between the intermolecular vector and the preferred direction.

Whereas in our ideal nematic system the order parameters (S=1) do not come into play, all two-particle functions depend only on the intermolecular separation r and the angle θ. Series expansion in terms of Legendre polynomials is recommended.

The first step is the separation of the Gay-Berne potential into a purely repulsive reference potential u0 and an attractive perturbation u1. By perturbation theory we get the free energy in the first order and the pair correlation in zeroth order of the reference system u0. This seems to be sufficient because the structural properties are mainly determined by repulsive forces.

$$u0(1,2)=\varepsilon(\theta)*[(r/\sigma_0-\sigma_p(\theta)+1)^{-12}-(r/\sigma_0-\sigma_p(\theta)+1)^{-6}+0.25] \quad r<r_m \quad \text{soft repulsion}$$

$$u0(1,2)=0 \quad r>r_m$$

$$u1(1,2)=-\varepsilon(\theta)/4 \quad r<r_m \quad \text{perturbation}$$

$$u1(1,2)=\varepsilon(\theta)*[(r/\sigma_0-\sigma_p(\theta)+1)^{-12}-(r/\sigma_0-\sigma_p(\theta)+1)^{-6}] \quad r>r_m,$$

$r_m = \sigma_0*[\sigma_p(\theta)+2^{1/6}-1]$ - position of the potential minimum.

The blip-function theory of Andersen, Weeks and Chandler (AWC)[4] provides a connection between the properties of hard spheres and soft spheres. We apply this theory to our system of parallel oriented, anisotropic molecules. In the frame work of the blip-theory we approximate the soft interaction potential u0(1,2) by an appropriate hard-core interaction between ellipsoids of revolution with the help of a perturbation method. The hard-core interaction is described by the Gaussian overlap model of Berne and Pechukas[8]. The socalled blip-integral represents the 1.order correction to the free energy of our reference system of hard ellipsoids. This term vanishes if the ellipsoidal parameters are chosen properly. Therefore we get for the free energy $A_0 = A^{hc}_{\parallel}$ which is correct up to the order ζ^1 (ζ is a small parameter describing the softness of the potential). The correlations are expressed in terms of the background correlation function, for which we get $y_0 = y^{hc}_{\parallel}$ (correct to the order ζ^2).

There are several possibilities to get a vanishing blip-integral. We have investigated the following methods:

I) variation of the ellipsoidal axes a and c for a given axial ratio, for example $c/a=\sigma_2/\sigma_1$

II) variation of the c-axis for a given value of the a-axis, therefore in general $c/a \neq \sigma_2/\sigma_1$.

This procedure is performed for all interesting values of temperature and density. So we get the free energy of the soft potential u0 and the y-correlations $y_0(1,2)=y_{hc}(1,2)$ in terms of the system of hard ellipsoids. The free energy of our reference system of hard

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ellipsoids, can be determined from the Carnahan-Starling equation of state. The correlations of of the hard-sphere system we determine from the solutions of the Percus-Yevick integral equations as given by Perram[5] and correct they according to Verlet, Weis[6] for the non-overlapping region and according to Grundke and Hendersen[7] for the overlapping region. The pair correlation of the total system is now given by

$$g(1,2)=g_0(1,2)=g_0(r,\cos\theta)=y^{hc}_{\parallel}(r,\cos\theta)*\exp(-\beta*u0(r,\cos\theta))$$

and for the free energy we get

$$A_{GB}=A^{hc}_{\parallel}+\pi\rho N*\int\int u1(r,\cos\theta)*y^{hc}_{\parallel}(r,\cos\theta)*\exp(-\beta*u0(r,\cos\theta))r^2 d\cos\theta\, dr\ .$$

Throughout this paper we have assumed for the parameters of the Gay-Berne potential the following values $\sigma_1/\sigma_0 = 1.0909$, $\varepsilon_s/\varepsilon_e = 5.0$ and $1/(\beta*\varepsilon_0) = 0.95$.

RESULTS

The pair correlation function of our perfectly oriented Gay-Berne system is given as the product of the background correlation function of the system of perfectly ordered hard ellipsoids $y^{hc}_{\parallel}$ and the Boltzmann factor of the reference system u0.

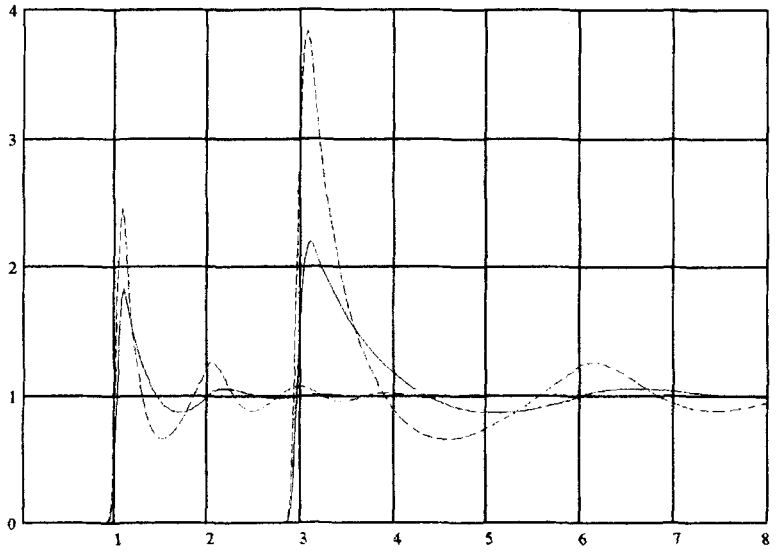

FIGURE 1 Longitudinal $g(\theta=0)$ and transversal $g(\theta=\pi/2)$ correlations for different values of the reduced density, solid lines: $\rho\sigma_0^3=0.181$, dashed lines: $\rho\sigma_0^3=0.28$; intermolecular separation in units of σ_0.

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In figure 1 the pair correlation function is displayed in direction parallel ($\theta=0$) and orthogonal ($\theta=\pi/2$) to the nematic director for two different densities and $c/a=\sigma_2/\sigma_1=3.0$. Surprisingly the longitudinal correlations ($\theta=0$) show a higher first neighbour peak than the transversal correlations ($\theta=\pi/2$). This is due to the different scaling behaviour of the background correlations and the Boltzmann factor. Whereas the r-dependence of the correlation function y^{hc}_{ij} scales according to the contact distance of the ellipsoid of revolution, this is not true for the Boltzmann factor and therefore not for their product.

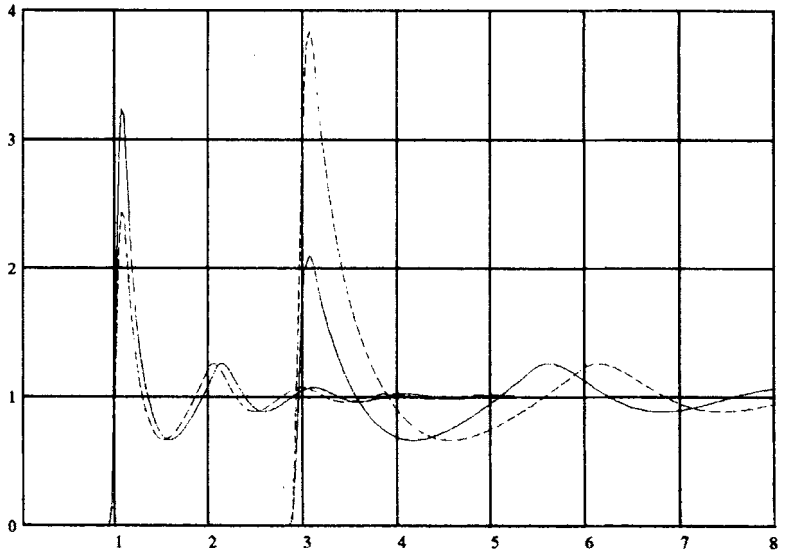

FIGURE 2 Longitudinal $g(\theta=0)$ and transversal $g(\theta=\pi/2)$ correlations calculated via different methods of nullifying the blip-integral; dashed lines: method I, $c/a=\sigma_2/\sigma_1=3.0$; solid lines: method II, a=const., a/s0=1.0455 (arbitrary assumption), c/a=2.628; reduced density $\rho\sigma_0^3=0.28$.

If we apply method II) for nullifying the blip-integral and choose $c/a=2.628<\sigma_2/\sigma_1$, then the transversal correlations are favoured (figure 2). Due to the finite range of the u0-potential the higher order peaks have equal heights for different θ values.
In figure 3a the projection $h_0(r)$ of the total correlation function $h(1,2)=g(1,2)-1$ is to be seen. The double peak is assumed to be the result of the preference of the longitudinal correlations for $c/a=\sigma_2/\sigma_1=3.0$. The corresponding structure factor $S_0(k)$ is displayed in figure 3b.

$S_0(k)=1+\rho\sigma_0^3 * \hat{h}_0(k)$, where $\hat{h}_0(k)$ is the Fourier transform of the component $h_0(r)$.

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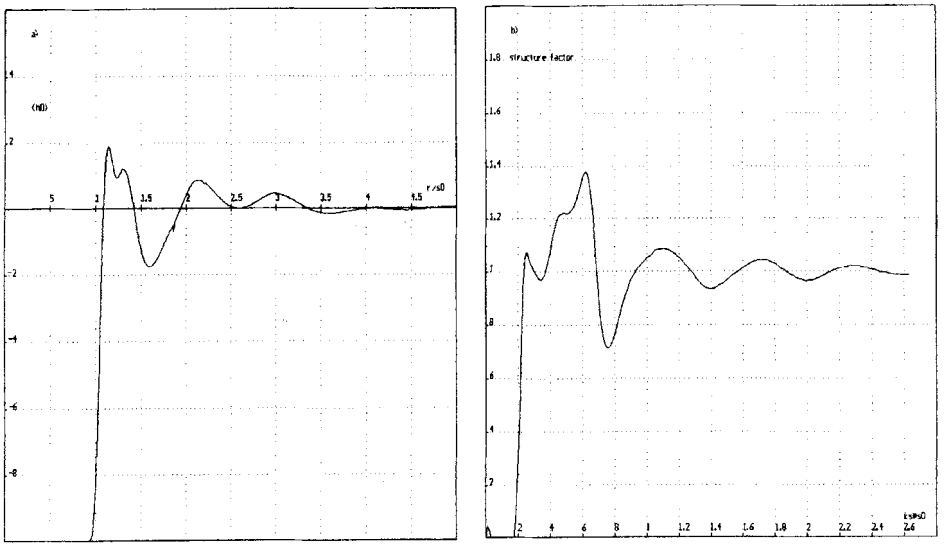

FIGURE 3 Projection $h_0(r)$ of the total correlation function (3a) and the corresponding structure factor (3b) at the reduced density $\rho\sigma_0^3=0.28$ determined with an axial ratio $c/a=\sigma_2/\sigma_1=3.0$.

The main peak occurs exactly at the wave vector $k_m=2\pi/\sigma_0$. The shoulder at $k_m/3$ can be related to the long axis of the molecule.

In figure 4 we display the compressibility factor $\beta P/\rho$ versus the reduced density. We calculate the presure via the free energy. For comparison the molecular dynamics results of the general Gay-Berne model (without orientational restrictions) of de Miguel et. al.[9] and the Percus-Yevick results for hard ellipsoids of revolution of Perera, Kusalik and Patey[10] are displayed.

DISCUSSION

The resulting axial ratio of the hard ellipsoid of revolution c/a significantly determines the structural properties of our Gay-Berne model. Further investigations are necessary to decide the question of which hard-core axial ratio best represents the given Gay-Berne potential. The axial ratio c/a has only minor influence on the thermodynamic pressure , which is mainly determined by the packing fraction.

The considerably lower compressibility factors of our restricted Gay-Berne model in comparison to the general one are due to the perfect orientational order of the molecules.

In calculating the pressure via the free energy we applied the method of Boublik and Diaz Pena[11] because the hard repulsion was described by the Gaussian overlap model.

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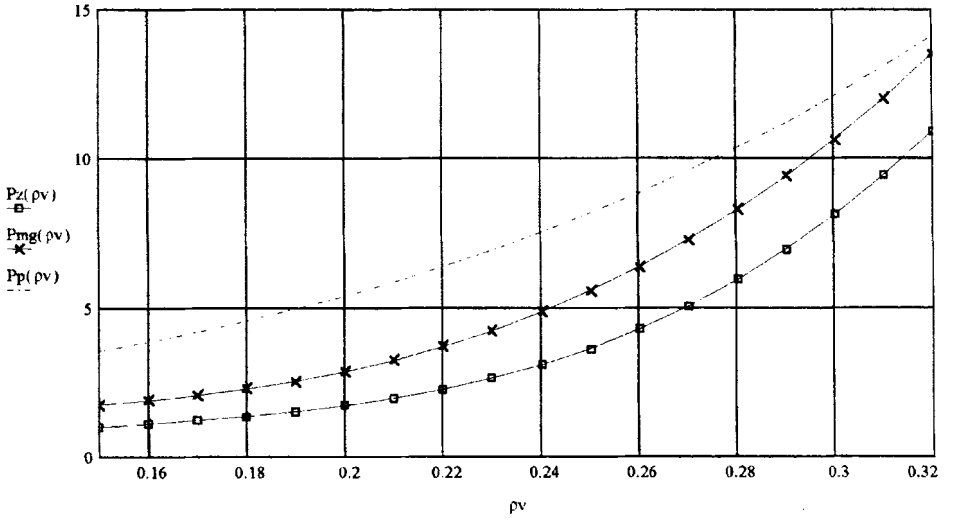

FIGURE 4 Compressibility factors $\beta P/\rho$ versus reduced density $\rho\sigma_0^3$; Pz-pressure via free energy (ideal nemat), $c/a=\sigma_2/\sigma_1=3.0$; Pmg: molecular dynamics result of de Miguel et al. for the general Gay_berne model; Pp: PY-theory of hard ellipsoids of revolution, virial equation (Perera, Kusalik, Patey).

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