Nematic-isotropic transition in a density-functional theory for hard spheroidal colloids

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Abstract

We introduce a density-functional formalism based on the Parsons-Lee and the generalized van der Waals theories in order to describe the thermodynamics of anisotropic particle systems with steric interactions. For ellipsoids of revolution, the orientational distribution function is obtained by minimizing the free energy functional and the equations of state are determined. The system exhibits a nematic-isotropic discontinuous transition, characterized by a phase separation between nematic and isotropic phases at finite as well low packing fractions. The model presents a phase behavior which is in good agreement with Monte-Carlo simulations for finite aspect ratios.

1 Introduction

Anisotropic bodies interacting through steric potentials exhibit a complex phase behavior which is the result solely of entropic effects [1–4]. Many theoretical investigations have been developed in order to understand the macroscopic properties of non-spherical particle systems at equilibrium. Hard spherocylinders present isotropic fluid and solid phases, which are also expected to be stable in one-component hard spheres [5], in addition to liquid crystal phases, such as nematic and smectic structures [10]. Ellipsoids of revolution with steric interactions can give rise to isotropic, nematic and various solid phases [11–13], but there exist doubts if such system may have stable smectic phase [14,15]. Hard convex polyhedra may exhibit crystal structures, plastic crystals and liquid-crystalline phases depending on the anisotropic shape of particles [4].

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Besides the theoretical interest, there are various experimental results on non-spherical bodies systems. Colloidal silica rodlike particles exhibit nematic and smectic phases depending on the volume fraction and aspect ratio [16]. Suspensions of gibbsite platelets are found to present a nematic-isotropic phase coexistence as the volume fraction is varied [17]. Goethite nanorods have shown nematic mesophases with very interesting magnetic properties [18]. These results suggest that mineral colloidal particles are promising materials for the study of liquid-crystalline phases [19].

One of the simplest model for colloidal anisotropic particles is the second-virial truncated free energy introduced by Onsager [20]. According to his calculations, the Helmholtz free energy can be written in the framework of a density-functional theory (DFT). For hard rodlike bodies, the model presents an entropy-driven nematic-isotropic (NI) discontinuous transition. However, Onsager’s theory requires very low concentrations to describe quantitatively the phase behavior of the system. Also, particles should be very long in order justify the truncation of the virial series at the second virial coefficient [20,21]. Clearly, these assumptions can make comparison with the experiments and simulations a difficult task.

Many different DFT have been developed for systems of anisotropic particles with realistic dimensions and at finite volume fractions [1,6–10]. A very successful proposal was presented by Parsons [8] and Lee [9], based on the idea that it is possible to decouple effectively the orientational and translational degrees of freedom. The Parsons-Lee (PL) theory leads to a configurational free energy which is a product of two terms, one is related to an hard-sphere (HS) reference system and other associated with the pair excluded volume. The HS system is usually described by the Carnahan-Starling (CS) theory [26], which gives an analytical expression for the equation of state in a good agreement with virial expansions. For hard spherocylinders [9] and hard spheroids [9], PL scheme gives a NI transition consistent with Monte-Carlo (MC) simulations even for short aspect ratios. Also, the theory recovers the Onsager’s model [20] for very long rods at low densities.

Although the CS equation of state is chosen to model the system of hard spheres, it is known that there exist many alternative proposals [22,25] for dense isotropic fluids. A physically insightful approach is presented by Nordholm et al. [24] and Freasier et al. [25], which calculated the configurational free energy by using a generalized van der Waals (GvdW) approximation [22]. This theory argues heuristically that the partition function is associated with the free volume, which is the volume available to particles in the system. In fact, the free volume is estimated through an interpolation between the simple van der Waals (vdW) theory, which is appropriate for diluted systems, and a GvdW scheme constructed to model high density limit. Nordholm et al. [24] shown that, for a uniform HS fluid, the GvdW theory leads to an equation of state that is consistent with CS approximation at finite densities. Freasier et al. [25] found good agreements in the oscillatory behavior of
the HS radial distribution function calculated by means of GvdW scheme. These results indicates that the GvdW theory is a reasonable approximation in order to investigate systems of hard spheres at least qualitatively.

We are interested in anisotropic fluid phases at finite as well high densities. Due to the importance and successful results, we do believe there is still room for studying the NI transition by means of a PL scheme. Specially, by means of alternative models for the reference system of hard spheres. In this work, we introduce a PL theory where the HS system is described by the GvdW theory developed by Nordholm et al. [24] and Freasier et al. [25]. We write a simple expression for free energy functional in terms of the orientational distribution function. The equations of state are calculated exactly and the phase behavior is determined. Comparison with MC results [32] shows that the model underestimates the NI transition for finite packing fractions. However, the theory agrees qualitatively well with the original PL theory and the simulation data for finite aspect ratios.

The paper is organized as follows. In Sec. 2 we introduce the free energy functional along the lines of PL and GvdW theories. Considering hard spheroids, the stationary distribution function is determined in Sec. 3. The equations of state are calculated in Sec. 4 as well the phase behavior in terms of the packing fraction and the axial ratio. Finally, we present our conclusions in Sec. 5.

2 Free energy functional

Consider a system of interacting rigid convex bodies, where \( \mathbf{q}_i \) is the generalized coordinate of particle \( i \), specifying the position of the center of mass and the orientation of the body-fixed frame. DFT formalism [1] establishes that we can write the configurational Helmholtz free energy as

\[
F[\varrho] = F_{id}[\varrho] + F_{ex}[\varrho],
\]

which is a functional of the number density \( \varrho(\mathbf{q}) \) such as

\[
N = \int d\mathbf{q} \varrho(\mathbf{q}),
\]

is the number of particles occupying the volume \( V \), \( F_{id} \) is the ideal part and \( F_{ex} \) is the excess part, which presents all contributions related with particle interactions.

We are interested in spatially homogeneous phases in an ensemble of cylindrically symmetric bodies. Then, the local number density can be written as

\[
\varrho(\mathbf{q}) = \rho f(\hat{\mathbf{a}}),
\]
where \( \rho = N/V \) and \( f(\hat{a}) \) is the probability density of finding a particle with orientation given by \( \hat{a} \). Consequently, the ideal free energy is given by

\[
F_{id} = NkT \left[ \ln \rho - 1 + \int d\hat{a} f(\hat{a}) \ln f(\hat{a}) \right],
\]

which is related to the translational and orientational entropies. The main problem is to determine a reasonable good approximation for the excess free energy, since it is very difficult to deal with the statistical mechanics of hard particle systems.

Here, we follow the PL theory \cite{1,8,9}, which basically states that the excess free energy can be approximated to

\[
F_{ex} = NkT \frac{J(\eta)}{8v_0} \int d\hat{a} d\hat{a}' f(\hat{a}) f(\hat{a}') V_c (\hat{a}, \hat{a}'),
\]

where \( J(\eta) \) is a function of the packing fraction \( \eta = \rho v_0 \), \( v_0 \) is the particle volume and \( V_c (\hat{a}, \hat{a}') \) is the excluded volume associated with a pair of particles oriented along \( \hat{a} \) and \( \hat{a}' \), respectively. The quantity \( J(\eta) \) should be chosen as the dimensionless free energy per particle of hard-sphere system. Usually, as Parsons \cite{8} and Lee \cite{9} did, \( J(\eta) \) is given by

\[
J_{CS}(\eta) = \frac{(4 - 3\eta) \eta}{(1 - \eta)^2},
\]

which leads to the well-known CS equation of state \cite{1,26}. Clearly, that is the best choice to model a HS system. Adopting this approach, Lee shown \cite{9} that a system of hard ellipsoids of revolution presents a NI transition which agrees with MC simulations \cite{11,12} for finite densities and aspect ratios.

However, it is perfectly possible to use another expression for \( J \) which describes the reference system of HS. This suggests we can adopt an alternative PL scheme in order to study the NI transition at finite densities. An interesting proposal for the free energy \( J \) is presented by Nordholm \textit{et al.} \cite{24} and Freasier \textit{et al.} \cite{25} through a GvdW theory. According to this theory, the partition function is related to the free volume fraction \( \Phi \) available to particles, which is estimated approximately. As a result, GvdW approach gives

\[
J^{GvdW}(\eta) \equiv - \ln \Phi = - \frac{2\pi}{3} \ln \left( 1 - \frac{6\eta}{\pi} \right).
\]

For diluted systems, this expression is consistent with the simple vDW theory,

\[
J^{vdW}(\eta) = - \ln (1 - 4\eta).
\]

Despite the fact that the model presents a mean-field character, GvdW approximation agrees qualitatively very well with the free volume fraction associated with the CS equation of state, as shown in Fig.\cite{1}.
Figure 1: Free volume fraction $\Phi$ as a function of the packing fraction $\eta$ for a system of hard spheres. vdW: van der Waals. GvdW: generalized van der Waals. CS: Carnahan-Starling.

Thus, we introduce a DFT considering that the excess free energy is given by Eq. (5) in addition to the function $J(\eta)$ in Eq. (7). Clearly, by construction, we find a excess free energy which is consistent with Nordholm et al. [24] and Freasier et al. [25] for a system of HS at finite packing fractions. Also, it is possible to check that, at very low densities, we obtain an expression which is in agreement with Onsager’s model [20] for hard rods,

$$F_{ex}^{On} = N\rho kT \int d\hat{a}d\hat{a}' f(\hat{a})f(\hat{a}')V_e(\hat{a},\hat{a}') .$$

(9)

3 Stationary distribution function for a system of hard spheroids

The total free energy (1) is written as the sum of the ideal part (4) and the excess part (5). Consequently, the PL theory leads to the dimensionless free energy density

$$\mathcal{F} \equiv \frac{F}{kTV} = \rho \ln \rho - \rho + \rho \left\{ \int d\hat{a} f(\hat{a}) \ln f(\hat{a}) + \frac{J(\eta)}{8\nu_0} \int d\hat{a}d\hat{a}' f(\hat{a})f(\hat{a}')V_e(\hat{a},\hat{a}') + \lambda \left[ \int d\hat{a} f(\hat{a}) - 1 \right] \right\} .$$

(10)

Note that we introduce the Lagrange’s multiplier $\lambda$ due to the normalization constraint

$$\int d\hat{a} f(\hat{a}) = 1.$$  

(11)
The free energy \( f \) can be used to describe dense fluid phases in a PL treatment regardless the quantity \( J \) for the HS reference system.

The equilibrium distribution \( f_{eq}(\hat{a}) \) is the one which minimizes the free energy density. This means that we should find the stationary distribution associated with \( f \). The constant \( \lambda \) is eliminated by using the normalization condition \( \int d\hat{a} f(\hat{a}) = 1 \). Then, we have a variational problem which leads to an Euler-Lagrange equation. As a result, the stationary distribution function may be written as

\[
f(\hat{a}) = \frac{1}{Z} \exp \left[ -\frac{J(\eta)}{4v_0} \int d\hat{a}' f(\hat{a}') V_e(\hat{a}, \hat{a}') \right],
\]

\[
Z = \int d\hat{a} \exp \left[ -\frac{J(\eta)}{4v_0} \int d\hat{a}' f(\hat{a}') V_e(\hat{a}, \hat{a}') \right].
\]

For a pair of hard spheroids, the excluded volume is a function of the relative orientation given by \( \cos^{-1}(\hat{a} \cdot \hat{a}') \). In practice, it is very difficult to write \( V_e \) in a simple form \[27\]. However, we consider an approximation by taking the Legendre expansion of the excluded volume up to the second order,

\[
V_e(\hat{a}, \hat{a}') = v_0 \left[ a_0 - a_2 P_2(\hat{a} \cdot \hat{a}') \right],
\]

where \( P_2 \) is the second Legendre polynomial. The coefficients \( a_0 \) and \( a_2 \) can be estimated, for example, by using pair configurations with known excluded volume expressions. Alternatively, we may determine the coefficient \( a_0 \) by taking the isotropic average of \( V_e \),

\[\langle V_e \rangle_{iso} = v_0 a_0,\]

which is proportional to the second virial coefficient in the isotropic phase. Also, for a pair of parallel spheroids, the excluded volume is \( 8v_0 \), which leads to

\[v_0 a_2 = \langle V_e \rangle_{iso} - 8v_0.\]

The isotropic average of \( V_e \), for general convex bodies \[28\], is given analytically by

\[\langle V_e \rangle_{iso} = 2v_0 + \frac{AM}{2\pi},\]

where \( A \) and \( M \) are the surface area and the mean curvature, respectively. All those shape measures can be written explicitly in terms of the spheroid axial ratio \( \kappa = a/b \).

4 Equations of states and phase behavior

It is straightforward to obtain expressions for the pressure \( P \) and the chemical potential \( \mu \) in a free energy density representation through the usual thermodynamic formalism \[29\]. We also may simplify the study by assuming that
only uniaxial nematic phases are described by the distribution function \( f(\hat{a}) \). That assumption is reasonable because statistical models for systems of axially symmetric bodies only give rise to uniaxial mesophases in the absence of external fields [30,31].

Then, using the total free energy density (10) and the distribution function (12), we can write the scaled pressure,

\[
P \equiv \frac{P v_0}{kT} = \eta + \frac{\eta^2}{8} \frac{\partial J}{\partial \eta} (a_0 - a_2 S^2), \tag{17}
\]

and the scaled chemical potential,

\[
\mu \equiv \frac{\mu}{kT} + \ln v_0 = \ln \eta + \frac{1}{8} \left( \eta \frac{\partial J}{\partial \eta} - J \right) \times (a_0 - a_2 S^2) - \ln Z, \tag{18}
\]

where \( S = \langle P_2 (\hat{a} \cdot \hat{n}) \rangle = \int d\hat{a} f(\hat{a}) P_2 (\hat{a} \cdot \hat{n}) \), \tag{19}

is the average of the second Legendre polynomial, and \( \hat{n} \) is the nematic director. For a given packing fraction \( \eta \), Eq.(19) is a self-consistent equation for \( S \), which may be solved numerically. After finding a solution, the pressure and the chemical potential are calculated and the thermodynamic stability of the system is determined. The equations of state are written in a way one can use any expression for the dimensionless free energy \( J \). Clearly, in this paper, we focus on the expressions (6) and (7) for \( J \).

![Figure 2: S parameter versus packing fraction \( \eta \) for axial ratio \( \kappa = 10 \). Black lines: stable solutions. Magenta dashed lines: non-stable solutions. Dots: MC simulations (A. Samborski et al. [32]).](image)

Fig. 2 shows the solutions of Eq.(19) for the axial ratio \( \kappa = 10 \). There are two stable branches (black lines), one associated with the isotropic phase.
\( S = 0 \) at low packing fractions, and other one related to a calamitic nematic phase \( S > 0 \) at high values of \( \eta \). There are also non-stable (metastable and unstable) solutions represented by magenta dashed lines. The isotropic branch becomes metastable as the packing fraction increases. A discotic phase \( S < 0 \) is presented at high \( \eta \), but it is non-stable. In fact, calamitic states are the only nontrivial solutions thermodynamically favorable. The order parameter behavior is in good agreement with the MC data results presented by Camp et al. [32].

The NI transition is discontinuous, with a density jump at the phase coexistence, as depicted in Fig. 3. Given a particular value of axial ratio \( \kappa \), the system goes from an isotropic phase \( I \) to a nematic phase \( N \) as the packing fraction increases. For very long spheroids \( \kappa \gg 1 \), we recover Onsager’s limit, characterized by long rodlike shapes and low densities. Also, it is possible to identify a Maxwell construction in a pressure versus volume graph. In fact, it is straightforward to show that the Maxwell construction is equivalent to the equilibrium conditions that characterizes the NI phase separation.

\[ \begin{align*}
\kappa &\quad \eta \\
5 &\quad 0.4 \\
10 &\quad 0.3 \\
15 &\quad 0.2 \\
20 &\quad 0.1 \\
25 &\quad 0.0 \\
30 &\quad 0.0
\end{align*} \]

Figure 3: Packing fraction \( \eta \) versus axial ratio \( \kappa \) for a system of hard spheroids. \( I \): isotropic. \( N \): nematic. Orange region: NI phase coexistence.

The usual PL theory adopts a CS equation of state for the hard-sphere reference system (PL-CS). The approach we propose here follows the main ideas of the PL scheme, but the system of hard spheres is described by an generalized van der Waals approximation (PL-GvdW). It is important to compare both models, since we introduce an alternative approach to the NI transition. We can do that by studying the equation of state in the vicinity of the phase transition. For example, the equilibrium pressure behavior is presented in Fig. 4 for axial ratio \( \kappa = 10 \). The PL-GvdW leads to a pressure transition higher than PL-CS results. However, both treatments seem to agree qualitatively well for the given axial ratio.

Also, it should be interesting to compare the results with approaches
PL-GvdW: Parsons-Lee theory with generalized van der Waals approximation. PL-CS: Parsons-Lee theory with Carnahan-Starling approach.

which consider fluctuations more appropriately, since we have a theory of mean-field type. Fig. 5 shows the $P \times \kappa$ phase diagram according to the DFT presented in this work, the usual PL-CS theory and the MC simulations from Camp et al. [32]. Our mean-field model underestimates the phase boundary for the packing fraction range considered compared with MC data. However, PL-GvdW leads to a phase boundary which agrees very well with PL-CS. This surprisingly result clearly shows the robustness of the decoupling approximation which characterizes the PL theory.

The CS equation of state is one of the best approximations for studying HS systems. However, the GvdW scheme, based on heuristic arguments, also leads to reasonable good results. Using a GvdW approximation, we have a
DFT which describes qualitatively well the phase behavior of anisotropic fluids at finite densities. Then, despite the simplicity, we argue that PL theory combining with GvdW approach can be useful to study hard-core effects in systems of convex non-spherical bodies.

5 Conclusions

We present a DFT constructed by using the Parsons-Lee theory and a generalized van der Waals approximation in order to investigate systems of hard anisotropic bodies. For the case of spheroidal shapes, the pair excluded volume is approximated to a truncated Legendre expansion, which simplifies the analysis. The model exhibits a NI discontinuous transition characterized by a phase coexistence. The isotropic phase is stable at low densities and the nematic phase becomes thermodynamically favorable as the packing fraction increases. The theory agrees qualitatively with MC results for finite axial ratios. Then, we believe the model is appropriate to study the macroscopic properties of non-spherical particle systems with steric interactions. Further investigations may consider the inclusion of attractive pair potentials, which may lead to a kind of van der Waals equation of state for a system of anisotropic molecules, as well to a richer phase behavior. From the statistical mechanics point of view, the model can also be extended to include disordered degrees of freedom in order to mimic shape variation effects, for example, in multicomponent mixtures.

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