North-Holland

DIRECT CORRELATION FUNCTION OF A ONE-DIMENSIONAL NEMATIC FLUID

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The direct correlation function of a fluid of aligned planar hard convex orientable bodies is determined exactly using a simple form for the separation of the centers at contact. An approximate analytical proposal for the direct correlation function in terms of a reference direct correlation function of a fluid of spherical molecules is shown to lead to the exact equation of state in the high-pressure limit.

1. Introduction

Certain organic liquids have structural order between that of conventional liquids and solids. The term nematics [1] refers to liquids which are positionally disordered but orientationally ordered, the most obvious way to achieve this orientational order being for the liquid to consist of nonspherical molecules. In the low temperature nematic phase the elongated constituent molecules are preferentially aligned along some director vector. At higher temperatures the orientational order disappears and nematics undergo a transition to an isotropic phase. Computer simulations [2] show that systems of hard convex elongated bodies reproduce these liquid crystalline phases and they are now being used as reference model systems to elucidate in a fundamental way the properties of more realistic systems.

The first principles statistical mechanical description of the equilibrium behaviour of fluids consisting of hard convex nonspherical molecules is not at present sufficiently advanced and analytical methods proposed for its study usually represent extensions of those developed for simple fluids. The main advantage of the hard convex body models is that the geometry of a pair of such objects is quite well known. In particular, the second virial coefficient can be expressed analytically for two- [3] and three-dimensional [4] fluids. However, higher virial coefficients can only be determined from numerical compu-

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tations [5] and semiempirical formulas [4]. Geometrical excluded volume considerations are reduced to finding the distance between the centers of two bodies at contact. This is a very complicated problem and approximate analytical expressions for it, such as the Gaussian overlap method [6], have been extensively considered in the literature. Moreover virial expansions and their resummations are used in this traditional approach of statistical mechanics to derive thermodynamic expressions for, e.g., the equation of state.

The density functional theory [7] has been recently applied to the study of systems of hard convex bodies. Hard-ellipsoid [8] and hard-ellipse [9] model systems have been considered in connection with the isotropic–nematic transition. In this modern approach to equilibrium statistical mechanics a privileged role is played by the Ornstein–Zernike direct correlation function [10] from which all the relevant thermodynamic quantities can be inferred. The direct correlation function of a system of nonspherical molecules is usually expressed in terms of some reference direct correlation function of a fluid of spherical molecules. This ad hoc approximation was introduced some years ago [11] in order to take advantage of the well-known analytical solution [12, 13] of the Percus–Yevick equation [14] for hard spheres and was then worked out numerically [15] with good results. To our knowledge, this approximation has never been tested analytically even for simple model systems.

In this paper we examine the *structural* properties of a model system of aligned planar hard convex nonspherical bodies and we find the exact expression for the direct correlation function. This work was prompted by a previous investigation [16] concerning the thermodynamic properties of some one-dimensional model systems. The different approximate forms for the direct correlation function used in the literature [8, 11] are compared next with our exact form and the effect of the approximations on the equation of state is investigated. A new analytical expression for the direct correlation function in terms of a reference direct correlation function of a fluid of spherical molecules is proposed and shown to be exact in the high-pressure limit and to yield good results for finite pressures.

2. Thermodynamics

We consider a system of N planar identical convex bodies moving in a plane with their centers of symmetry restricted to lie on a line. We label the ith body ($i = 1, 2 \ldots, N$) by the position x_i ($0 \leq x_i \leq L$) of its center of symmetry and by its orientation θ_i with respect to the normal to the line of centers. We assume nearest-neighbor hard-core interactions depending on the separation of centers at contact $\sigma(\theta, \theta')$ (see fig. 1), i.e.

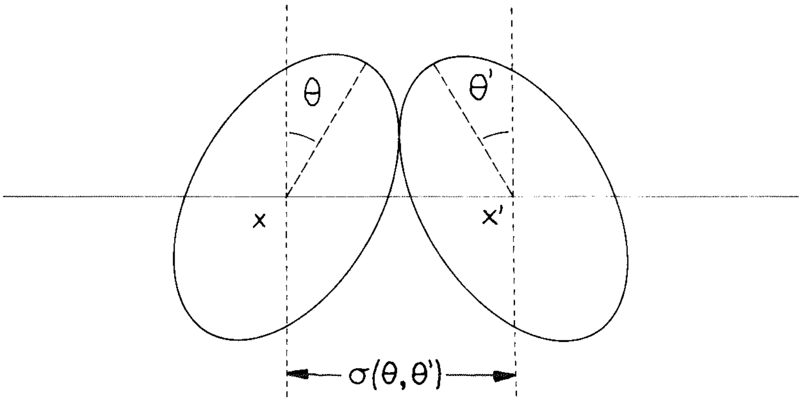

Fig. 1. A diagram illustrating the separation of centers at contact $\sigma(\theta, \theta')$ of two planar convex bodies.

$$\phi(x, \theta; x', \theta') = \begin{cases} \infty, & |x - x'| < \sigma(\theta, \theta'), \\ 0, & |x - x'| > \sigma(\theta, \theta'). \end{cases} \tag{1}$$

As the precise determination of $\sigma(\theta, \theta')$ is a complicated geometrical problem we limit henceforth our study to the simplest (unrealistic) form of $\sigma(\theta, \theta')$ which permits to solve the thermodynamics and structure of the system. In particular, we consider that $\sigma(\theta, \theta')$ can be written as

$$\sigma(\theta, \theta') = \tfrac{1}{2}[\sigma(\theta) + \sigma(\theta')], \tag{2}$$

where $\sigma(\theta)$ is an arbitrary positive function of θ.

As explained elsewhere [16] this approximation leads to a factorizable transfer operator in the isobaric ensemble with a unique eigenvalue λ which is simply related to the chemical potential $\mu(P)$ by $\beta\mu(P) = -\log \lambda$, where $\beta = 1/k_B T$ is the inverse temperature and P the pressure. The equation of state is then given by

$$\frac{1}{n} = \frac{\partial \mu(P)}{\partial P} = \frac{1}{\beta P} + \langle \sigma(\theta) \rangle, \tag{3}$$

where n is the average number density and $\langle \cdots \rangle$ denotes the average over the angular distribution function

$$h(\theta) = \frac{\exp[-\beta P \sigma(\theta)]}{\int_{-\pi}^{\pi} d\theta \exp[-\beta P \sigma(\theta)]}. \tag{4}$$

For aligned hard disks of diameter σ eq. (2) is exact with $\sigma(\theta)=\sigma$ and eq. (3) yields $1/n=\sigma+1/\beta P$, i.e., the equation of state of a hard-rod fluid.

For orientable bodies with a center of symmetry we clearly have $\sigma(\theta, \theta')=\sigma(-\theta, -\theta')$ and $\sigma(\theta \pm \pi, \theta')=\sigma(\theta, \theta')=\sigma(\theta, \theta' \pm \pi)$ and from eq. (2) a general parametrization of $\sigma(\theta)$ can be given as $\sigma(\theta)=\Sigma_{m=0}^{\infty} a_{2m} T_{2m}(\cos\theta)$, where $T_m(\cos\theta)=\cos(m\theta)$ are the Chebyshev polynomials [17]. Although the geometry has been strongly hidden in eq. (2) the coefficients a_{2m} in the polynomial expansion can be related to some general properties. For example, if we consider a system of aligned hard ellipses with minor axis σ and major axis $\kappa\sigma$, κ being the aspect ratio ($\kappa>1$) and if θ denotes the angle between the major axis and the normal to the line of centers then we have $\sigma(0,0)=\sigma$ and $\sigma(\pi/2, \pi/2)=\kappa\sigma$. Hence $a_0=\frac{1}{2}\sigma(\kappa+1)$ and $a_2=-\frac{1}{2}\sigma(\kappa-1)$ if we assume for $\sigma(\theta)$ the simplest form $\sigma(\theta)=a_0+a_2\cos(2\theta)$. The angular distribution function $h(\theta)$ reads in this case

$$h(\theta)=\frac{1}{2\pi}\,\frac{\exp[\frac{1}{2}\beta P\sigma(\kappa-1)\cos(2\theta)]}{I_0(\frac{1}{2}\beta P\sigma(\kappa-1))}\,, \tag{5}$$

where $I_n(x)$ is the nth order modified Bessel function [17]. Notice that this result corresponds to the one-order parameter approximation of $h(\theta)$ considered by Cuesta et al. [9] in their study of the two-dimensional isotropic–nematic transition of the unrestricted hard-ellipse fluid with $\gamma=\frac{1}{2}\beta P\sigma(\kappa-1)$ being the corresponding order parameter. With this choice of $h(\theta)$ the equation of state can be written from eq. (3) as

$$\frac{1}{n}=\frac{1}{\beta P}+\tfrac{1}{2}\sigma(\kappa+1)-\tfrac{1}{2}\sigma(\kappa-1)\,\frac{I_1(\frac{1}{2}\beta P\sigma(\kappa-1))}{I_0(\frac{1}{2}\beta P\sigma(\kappa-1))}\,. \tag{6}$$

This is precisely the equation of state derived by Lebowitz et al. [16] in a recent study of the thermodynamics of some orientable one-dimensional model systems. As explained there the limiting equation of state in which the ellipses are constrained to line up under high pressure has not the expected hard-rod form but rather

$$\lim_{P\to\infty}\frac{P}{P_0}=\frac{3}{2}\,, \tag{7}$$

where $P_0=n/\beta(1-n\sigma)$ denotes the pressure of a hard-rod fluid. Such a result is not specific of our model but can also be derived for aligned planar hard convex objects using more realistic forms of $\sigma(\theta, \theta')$ [16]. A similar behavior was previously reported by Frenkel [18] for an elongated ellipsoidal system.

3. Distribution functions

In this section we determine the one- and two-point distribution functions of the solvable model described by eq. (2). Our treatment is a generalization for nonspherical bodies of that of Percus [19]. Since the methodology is standard we merely gather here the main results.

The isobaric probability distribution function in phase space of a one-dimensional system of N identical bodies with an internal degree of freedom θ_i interacting through a nonspherical pair nearest-neighbor potential $\phi(y_i;\, \theta_{i-1}, \theta_i)$ is given by

$$w_N(\{y_i, \theta_i\}, P) = \frac{1}{Q_N(P)} \exp\left(-\beta \sum_{i=1}^{N} [\phi(y_i;\, \theta_{i-1}, \theta_i) + Py_i]\right), \tag{8}$$

where $y_i = |x_{i+1} - x_i|$ denotes the relative distance separating a pair of contiguous bodies and $Q_N(P)$ is the isobaric partition function

$$Q_N(P) = \prod_{i=1}^{N} \int_{-\pi}^{+\pi} \frac{\mathrm{d}\theta_i}{2\pi} \int_{0}^{\infty} \mathrm{d}y_i \exp\left(-\beta \sum_{i=1}^{N} [\phi(y_i;\, \theta_{i-1}, \theta_i) + Py_i]\right), \tag{9}$$

where a periodic boundary condition $x_{N+1} = x_1$ and $\theta_0 = \theta_N$ has been assumed. From eqs. (1) and (2) it is seen that the isobaric partition function $Q_N(P)$ factorizes and this then permits the exact determination of the one- and two-point distribution functions.

We start by considering the one-point distribution function or local number density

$$n(x, \theta) = \left\langle\!\!\left\langle \sum_{i=1}^{N} \delta(x - x_i)\, \delta(\theta - \theta_i) \right\rangle\!\!\right\rangle, \tag{10}$$

where $\langle\!\langle \cdots \rangle\!\rangle$ denotes the average over the isobaric probability distribution function $w_N(\{y_i, \theta_i\}, P)$. Whenever the system is translationally invariant, $n(x, \theta)$ is only a function of the orientation variable θ. Using eqs. (1), (2) and (8), (9) it can be readily found that for this case

$$n(x, \theta) = nh(\theta)\,, \tag{11}$$

with $h(\theta)$ given by eq. (4). For the system of aligned hard ellipses considered above, eqs. (5) and (11) show an orientational order (nematic phase), the angular distribution $h(\theta)$ being centered around $\theta = 0$ with a width which decreases as P or κ increase, β playing only the role of a scale factor.

Next, we consider the two-point distribution function

$$n_2(x, \theta; x', \theta') = \left\langle\!\!\left\langle \sum_{i=1}^{N} \sum_{i \neq j=1}^{N} \delta(x - x_i)\, \delta(\theta - \theta_i)\, \delta(x' - x_j)\, \delta(\theta' - \theta_j) \right\rangle\!\!\right\rangle . \quad (12)$$

Clearly, for translationally invariant systems $n_2(x, \theta; x', \theta') = n_2(x - x'; \theta, \theta')$. At this stage we shift our attention to the conditional probability density

$$g(x; \theta, \theta') = \left\langle\!\!\left\langle \delta(\theta' - \theta_N) \sum_{j=1}^{N-1} \delta(x - x_j)\, \delta(\theta - \theta_j) \right\rangle\!\!\right\rangle \quad (13)$$

for finding a body at a distance x from the origin (where the Nth body with orientation θ' is localized because of the periodic boundary conditions) and orientation θ. The determination of $g(x; \theta, \theta')$ is straightforward using eqs. (1), (2) and (8), (9). The analysis can be further simplified by introducing the Laplace transform $\hat{g}(q; \theta, \theta') = \int_0^\infty \mathrm{d}x \exp(-qx)\, g(x; \theta, \theta')$ to find in the thermodynamic limit

$$\begin{aligned}\hat{g}(q; \theta, \theta') &= \left\langle\!\!\left\langle \delta(\theta' - \theta_N) \sum_{j=1}^{\infty} \exp(-qx_j)\, \delta(\theta - \theta_j) \right\rangle\!\!\right\rangle \\ &= h(\theta)\, h_q(\theta) \frac{\beta P h(\theta)}{(\beta P + q) h_q(\theta) - \beta P h(\theta) \exp[-q\sigma(\theta)]} \\ &\quad \times \exp\{\beta P[\sigma(\theta) - \sigma(\theta')] - \tfrac{1}{2} q[\sigma(\theta) + \sigma(\theta')]\} ,\end{aligned} \quad (14)$$

where

$$h_q(\theta) = \frac{\exp[-(\beta P + q)\sigma(\theta)]}{\int_{-\pi}^{+\pi} \mathrm{d}\theta \exp[-(\beta P + q)\sigma(\theta)]} . \quad (15)$$

Because of the translational invariance,

$$n_2(x; \theta, \theta') = ng(x; \theta, \theta') = n^2 h(\theta)\, h(\theta')\, [\nu_2(x; \theta, \theta') + 1] , \quad (16)$$

where we have introduced the pair correlation function [20] $\nu_2(x; \theta, \theta')$ which can be related to the direct correlation function $c(x; \theta, \theta')$ through the Ornstein–Zernike equation. Since this equation takes a particularly simple form in the Fourier representation, we introduce the Fourier transform $\tilde{\nu}_2(k; \theta, \theta')$ which in a one-dimensional space can be written as: $\tilde{\nu}_2(k; \theta, \theta') = \hat{\nu}_2(+\mathrm{i}q; \theta, \theta') + \hat{\nu}_2(-\mathrm{i}q; \theta, \theta')$. For eqs. (4) and (14), (16) we obtain after a lengthy but simple calculation

$$\tilde{\nu}_2(k;\theta,\theta') = \lambda(k)\cos(\tfrac{1}{2}k[\sigma(\theta)+\sigma(\theta')]) - \mu(k)\sin(\tfrac{1}{2}k[\sigma(\theta)+\sigma(\theta')]) , \tag{17}$$

where

$$\lambda(k) = \frac{1}{n}\,\frac{u(k)}{[u(k)]^2 + [v(k)+w(k)]^2} \tag{18}$$

and

$$\mu(k) = \frac{1}{n}\,\frac{v(k)+w(k)}{[u(k)]^2 + [v(k)+w(k)]^2} \tag{19}$$

with

$$u(k) = \tfrac{1}{2}[1 - \langle \cos k\sigma(\theta)\rangle] , \tag{20}$$

$$v(k) = \tfrac{1}{2}\langle \sin k\sigma(\theta)\rangle , \tag{21}$$

$$w(k) = \tfrac{1}{2}\,\frac{k}{\beta P} . \tag{22}$$

Therefore, $\tilde{\nu}_2(k;\ \theta,\ \theta')$ has an oscillatory behavior with coefficients $\lambda(k)$ and $\mu(k)$ which depend on the angular distribution function through eqs. (20) and (21).

4. Direct correlation function

The traditional formulation of equilibrium statistical mechanics [20] deals with a set of n-point distribution functions of which the average density is the first member, the second (the pair correlation function) playing a central role for systems of bodies interacting through a pair interaction potential. The modern theoretical approach to equilibrium statistical mechanics uses instead the density-functional theory [7]. In this formulation a set of direct correlation functions are obtained by taking successive functional derivatives of the intrinsic Helmholtz free energy with respect to the local number density. The second member of this hierarchy, the Ornstein–Zernike direct correlation function [10], plays a role analogous to that of the pair correlation function in the traditional formulation. The link between both approaches is given by the Ornstein–Zernike equation.

For the model system considered in this paper, the Ornstein–Zernike equation reads in Fourier transform

$$\tilde{\nu}_2(k;\theta,\theta') = \tilde{c}(k;\theta,\theta') + n \int_{-\pi}^{+\pi} d\theta''\, h(\theta'')\, \tilde{\nu}_2(k;\theta,\theta'')\, \tilde{c}(k;\theta'',\theta') , \qquad (23)$$

where $\tilde{c}(k;\theta,\theta') = \int_{-\infty}^{+\infty} dx \exp(ikx)\, c(x;\theta,\theta')$ with $c(x;\theta,\theta')$ denoting the direct correlation function.

This functional equation has a degenerate kernel represented by

$$h(\theta'')\, \tilde{\nu}_2(k;\theta,\theta'') = \sum_{i=1}^{2} \alpha_i(\theta)\, \beta_i(\theta'') ,$$

the analytical expressions of $\alpha_i(\theta)$ and $\beta_i(\theta'')$ being easily determined from eqs. (4) and (17). Following the general theory of linear integral equations [21] the Ornstein–Zernike equation (23) reduces immediately to a system of two linear equations in two unknowns, leading to the following exact expression for $\tilde{c}(k;\theta,\theta')$:

$$n\tilde{c}(k;\theta,\theta') = -\frac{2\beta P}{k} \sin(\tfrac{1}{2}k[\sigma(\theta)+\sigma(\theta')]) - \left(\frac{2\beta P}{k}\right)^2 \sin(\tfrac{1}{2}k\sigma(\theta)) \sin(\tfrac{1}{2}k\sigma(\theta')) , \qquad (24)$$

which has a simpler structure than $\tilde{\nu}_2(k;\theta,\theta')$. The direct correlation function $c(x;\theta,\theta') = \int_{-\infty}^{+\infty} dk \exp(-ikx)\, \tilde{c}(k;\theta,\theta')$ can then be readily found by using the Heaviside step function

$$\Theta(x) = \begin{cases} 1 , & x > 0 , \\ 0 , & x < 0 . \end{cases} \qquad (25)$$

Clearly,

$$\int_{-\infty}^{+\infty} dx \exp(-ikx)\, \Theta(a - |x|) = \frac{2\sin(ka)}{k} . \qquad (26)$$

From eqs. (24) and (26) we immediately find, using elementary properties of the Fourier transforms, that

$$nc(x;\theta,\theta') = -\beta P \Theta(\tfrac{1}{2}[\sigma(\theta)+\sigma(\theta')] - |x|) - \beta^2 P^2 \int_{-\infty}^{+\infty} dx'\, \Theta(\tfrac{1}{2}\sigma(\theta) - |x'|)\, \Theta(\tfrac{1}{2}\sigma(\theta') - |x - x'|) , \qquad (27)$$

where the integral appearing in eq. (27) corresponds to the overlap length of the two step functions in the integrand. We thus get the following exact expression for the direct correlation function of the model system considered in this paper:

$$nc(|x|;\theta,\theta') = -\beta P\Theta(\tfrac{1}{2}[\sigma(\theta)+\sigma(\theta')]-|x|)$$
$$\times(1+\beta P\{\tfrac{1}{2}[\sigma(\theta)+\sigma(\theta')]-|x|\}\;\Theta(|x|-\tfrac{1}{2}|\sigma(\theta)-\sigma(\theta')|)$$
$$+\beta P\min[\sigma(\theta),\sigma(\theta')]\;\Theta(\tfrac{1}{2}|\sigma(\theta)-\sigma(\theta')|-|x|))\,, \tag{28}$$

which simplifies for aligned hard disks ($\sigma(\theta)=\sigma$) to

$$nc_0(|x|) = -\beta P\Theta(\sigma-|x|)\,[1+\beta P(\sigma-|x|)] \tag{29}$$

or, using the equation of state $1/n=\sigma+1/\beta P$, we have

$$c_0(|x|) = -\Theta(\sigma-|x|)\,\frac{1-n|x|}{(1-n\sigma)^2}\,, \tag{30}$$

which is the well-known expression for the direct corrleation function of a hard-rod fluid. We note from eq. (28) that $c(|x|;\theta,\theta')$ has the range of the separation of centers at contact $\sigma(\theta,\theta')$. We also remark that the terms containing the difference $|\sigma(\theta)-\sigma(\theta')|$ seem a bit artificial. These terms appear as a consequence of the separable form of $\sigma(\theta,\theta')$ considered in eq. (2) and can also be found in hard-sphere mixtures [4] (notice that our model is equivalent to a mixture of hard rods of continuously distributed diameters $\sigma(\theta)$).

We end this section by establishing the connection between the thermodynamics and the structure. This can be done for spherical molecules through the compressibility equation which relates the isothermal compressibility and the Fourier transform of the pair correlation function at zero wave vector. Then the Ornstein–Zernike equation permits to link the isothermal compressibility and the direct correlation function at zero wave vector. For anisotropic molecular fluids [22] an equation analogous to the compressibility equation relating the isothermal compressibility and the direct correlation function can be derived in a somehow more complicated form involving k-space harmonic coefficients. Here, we consider a simpler connection valid for the specific model considered in this paper.

Let us first integrate eq. (28) with respect to x to obtain

$$n\int_{-\infty}^{+\infty} \mathrm{d}x\; c(x;\theta,\theta') = -\beta P[\sigma(\theta)+\sigma(\theta')] - \beta^2P^2\sigma(\theta)\,\sigma(\theta')\,,$$

where we have used the identity

$$2\min[\sigma(\theta), \sigma(\theta')] = \sigma(\theta) + \sigma(\theta') - |\sigma(\theta) - \sigma(\theta')| .$$

Multiplying this result by $h(\theta)h(\theta')$ and integrating with respect to the orientational variables over the period $-\pi$ to $+\pi$ we have

$$n\int_{-\pi}^{+\pi} \mathrm{d}\theta\, h(\theta) \int_{-\pi}^{+\pi} \mathrm{d}\theta'\, h(\theta') \int_{-\infty}^{+\infty} \mathrm{d}x\, c(x; \theta, \theta')$$
$$= -2\beta P\langle\sigma(\theta)\rangle - \beta^2 P^2 \langle\sigma(\theta)\rangle^2 . \quad (31)$$

Thus, using eq. (3) we get

$$\left(\frac{\beta P}{n}\right)^2 = 1 - n\int_{-\pi}^{+\pi} \mathrm{d}\theta\, h(\theta) \int_{-\pi}^{+\pi} \mathrm{d}\theta'\, h(\theta') \int_{-\infty}^{+\infty} \mathrm{d}x\, c(x; \theta, \theta') , \quad (32)$$

relating the compressibility factor $\beta P/n = 1 + \beta P\langle\sigma(\theta)\rangle$ and the direct correlation function. Eq. (32) is exact for the model system considered in this paper. In the next section we introduce approximate proposals for the direct correlation function and find from eq. (32) the corresponding compressibility factors.

5. Approximate forms for the direct correlation function

The direct correlation function for hard nonspherical bodies has been expressed in the literature in terms of some reference direct correlation function of a fluid of spherical molecules [8, 9, 11]. In this section we review some of these approximations adapted to our specific model and compare them with the exact results of the preceding section.

Proposed originally by Pynn [11] a first approximate analytical expression for the direct correlation function of a fluid of hard anisotropic molecules is given by the Percus–Yevick result for hard spheres [12, 13] with the hard-sphere diameter appearing in the dimensionless distance x/σ replaced by an orientation-dependent diameter, namely, the center-to-center separation between two hard bodies at contact ($\sigma(\theta, \theta')$ in our model). When expressed in terms of x/σ, eq. (29) reads

$$nc_0(|x|) = -\beta P\Theta\left(1 - \frac{|x|}{\sigma}\right)\left[1 + \beta P\sigma\left(1 - \frac{|x|}{\sigma}\right)\right] . \quad (33)$$

Hence, Pynn's suggestion takes in the present case the form

$$nc(|x|;\theta,\theta') = -\beta P\Theta\left(1-\frac{|x|}{\sigma(\theta,\theta')}\right)\left[1+\beta P\sigma\left(1-\frac{|x|}{\sigma(\theta,\theta')}\right)\right], \tag{34}$$

where $\sigma=\sigma(0,0)$. Notice that $c(|x|;\ \theta,\ \theta')$ is unphysical at the origin since it has no orientational dependence there at all. As indicated by Lado [15] this is not an important flaw for a D-dimensional fluid ($D>1$) because one usually needs only the D-dimensional integral of the direct correlation function so that it will be multiplied by a power of the relative distance, a step which washes out the short-range structure of the direct correlation function. Indeed, Lado found a surprisingly good agreement between Pynn's approximation and the true Percus–Yevick solution for a model of hard dumbells. An elementary integration of eq. (34) leads to

$$n\int_{-\infty}^{+\infty}\mathrm{d}x\, c(|x|;\theta,\theta') = -2\beta P(1+\tfrac{1}{2}\beta P\sigma)\,\sigma(\theta,\theta')\,, \tag{35}$$

and using eqs. (2) and (32) we obtain an approximate compressibility factor given by

$$\begin{aligned}\left(\frac{\beta P}{n}\right)^2 &= 1+2\beta P(1+\tfrac{1}{2}\beta P\sigma)\langle\sigma(\theta)\rangle \\ &= [1+\beta P\langle\sigma(\theta)\rangle]^2+\beta^2P^2\langle\sigma(\theta)\rangle[\sigma-\langle\sigma(\theta)\rangle]\,.\end{aligned} \tag{36}$$

As $\langle\sigma(\theta)\rangle>\sigma$, Pynn's approximation underestimates the compressibility factor.

An alternative analytical proposal suggested by Baus et al. [8] in their study of the isotropic–nematic transition of a hard-ellipsoid system is based on the idea of factorizing the translational and angular variables in the direct correlation function. The translational part is given by the isotropic direct correlation function of a reference hard-sphere system, while the angular part is determined by the excluded volume of two hard bodies of given orientations averaged over the orientations of their center-to-center position and divided by the hard-sphere volume. Clearly, for aligned bodies the average over the center-to-center position is trivial and from eq. (33) the factorization approach of Baus et al. reduces for our one-dimensional system simply to

$$nc(|x|;\theta,\theta') = -\frac{\sigma(\theta,\theta')}{\sigma}\,\beta P\Theta\left(1-\frac{|x|}{\sigma}\right)\left[1+\beta P\sigma\left(1-\frac{|x|}{\sigma}\right)\right]. \tag{37}$$

In spite of the different approaches proposed by Baus et al. and Pynn the remarkable fact is that both suggestions lead to the same approximate compressibility factor (eq. (36)). This can be easily checked by a simple integration of eq. (37) using eqs. (2) and (32). In general, this equivalence with respect to the thermodynamics can be easily proved whenever the system is translationally invariant.

A new analytical proposal for the direct correlation function can be derived in view of eq. (28). As noted earlier, one might expect that terms containing the difference $|\sigma(\theta) - \sigma(\theta')|$ will not appear for realistic forms of the closest separation of centers. Taking hence $|\sigma(\theta) - \sigma(\theta')| \simeq 0$ in eq. (28) we get

$$nc(|x|; \theta, \theta') = -\beta P \Theta(\sigma(\theta, \theta') - |x|)\,[1 + \beta P(\sigma(\theta, \theta') - |x|)]\,, \tag{38}$$

which has the same structure as eq. (29) with σ replaced by $\sigma(\theta, \theta')$. However, this is not Pynn's proposal since eq. (38) now leads to an orientation-dependent direct correlation function also at the origin. When this approximation is combined with eqs. (32) and (2) we find

$$\begin{aligned}\left(\frac{\beta P}{n}\right)^2 &= 1 + 2\beta P\langle\sigma(\theta)\rangle + \tfrac{1}{2}\beta^2P^2[\langle\sigma^2(\theta)\rangle + \langle\sigma(\theta)\rangle^2] \\ &= [1 + \beta P\langle\sigma(\theta)\rangle]^2 + \tfrac{1}{2}\beta^2P^2[\langle\sigma^2(\theta)\rangle - \langle\sigma(\theta)\rangle^2]\,.\end{aligned} \tag{39}$$

Therefore, this proposal overestimates the compressibility factor by a term containing the mean square fluctuations of $\sigma(\theta)$.

We are now ready for a quantitative comparison of the various approaches considered in this section. Let us apply the above results to the fluid of aligned hard ellipses described by eq. (6) which is assumed henceforth to be exact. The two approximations (eqs. (34) and (38)) can be checked in detail by determining $\langle\sigma(\theta)\rangle$ and $\langle\sigma^2(\theta)\rangle$ over the distribution function given by eq. (5). In this particular case, Pynn's proposal leads to the following approximate compressibility factor:

$$\left(\frac{\beta P}{n}\right)^2 = 1 + P^*(1 + \tfrac{1}{2}P^*)\left(\kappa + 1 - (\kappa - 1)\,\frac{I_1(\bar{P})}{I_0(\bar{P})}\right), \tag{40}$$

where $P^* = \beta P\sigma$ and $\bar{P} = \frac{1}{2}P^*(\kappa - 1)$, while our proposal yields

$$\begin{aligned}\left(\frac{\beta P}{n}\right)^2 &= 1 + P^*\left(\kappa + 1 - \tfrac{5}{4}(\kappa - 1)\,\frac{I_1(\bar{P})}{I_0(\bar{P})}\right) \\ &\quad + \tfrac{1}{2}P^{*2}\left[\tfrac{1}{2}(\kappa + 1)^2 - (\kappa^2 - 1)\,\frac{I_1(\bar{P})}{I_0(\bar{P})} + \tfrac{1}{4}(\kappa - 1)^2\left(1 + \frac{I_1^2(\bar{P})}{I_0^2(\bar{P})}\right)\right].\end{aligned} \tag{41}$$

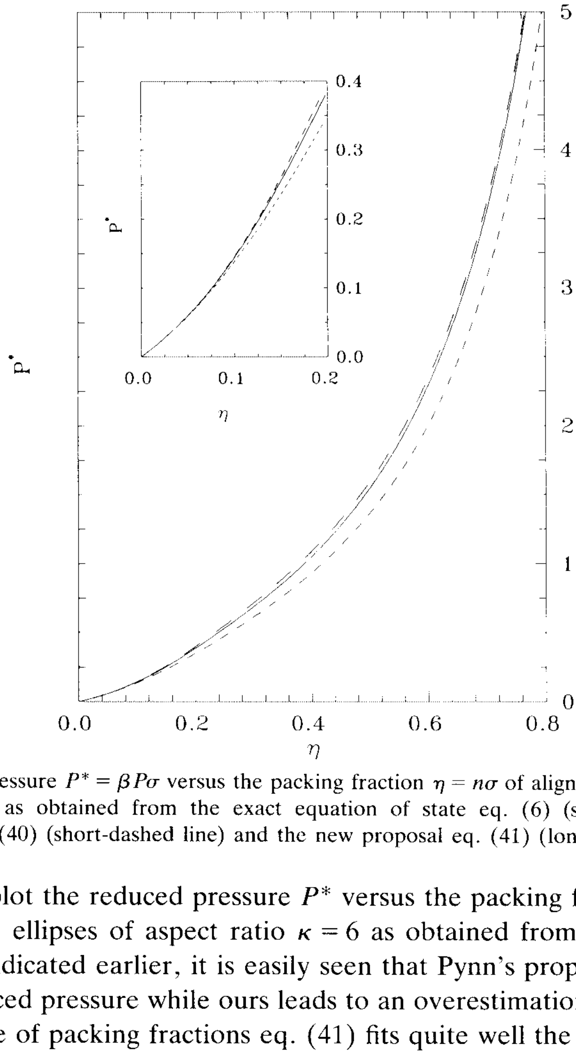

Fig. 2. Reduced pressure $P^* = \beta P \sigma$ versus the packing fraction $\eta = n\sigma$ of aligned hard ellipses of aspect ratio $\kappa = 6$ as obtained from the exact equation of state eq. (6) (solid line), Pynn's approximation eq. (40) (short-dashed line) and the new proposal eq. (41) (long-dashed line).

In fig. 2 we plot the reduced pressure P^* versus the packing fraction $\eta = n\sigma$ of aligned hard ellipses of aspect ratio $\kappa = 6$ as obtained from eqs. (6), (40) and (41). As indicated earlier, it is easily seen that Pynn's proposal underestimates the reduced pressure while ours leads to an overestimation. However, in the whole range of packing fractions eq. (41) fits quite well the exact equation of state.

For low densities we can expand the pressure into virial series $\beta P = \Sigma_{n=0}^{\infty} nB_n$ with B_n being the virial coefficients. Both approximations yield the same (exact) second virial coefficient $B_2 = \sigma(\kappa + 1)/2$. In table I we summarize the analytical expressions for the third and fourth virial coefficients where discrepancies arise.

Finally, we consider the limiting equation of state at high pressures. From eq. (40) it can be easily found that

$$\lim_{P\to\infty} \frac{P}{P_0} = \frac{5}{4} ,$$

Table I
Analytical expressions for the third and fourth virial coefficients as obtained from eq. (6) (exact), eq. (40) (Pynn) and eq. (41) (our new proposal).

Method \ Coefficient	B_3/σ^2	B_4/σ^3
exact	$\frac{1}{4}[(\kappa+1)^2 - \frac{1}{2}(\kappa-1)^2]$	$\frac{1}{8}(\kappa+1)[(\kappa+1)^2 - \frac{3}{2}(\kappa-1)^2]$
Pynn	$\frac{1}{8}[(\kappa+1)(\kappa+3) - (\kappa-1)^2]$	$\frac{1}{4}[(\kappa+1)^2 - \frac{1}{2}(\kappa+\frac{3}{2})(\kappa-1)^2]$
eq. (41)	$\frac{1}{4}[(\kappa+1)^2 - \frac{3}{8}(\kappa-1)^2]$	$\frac{1}{8}(\kappa+1)[(\kappa+1)^2 - \frac{5}{4}(\kappa-1)^2]$

in contradiction with the exact result in eq. (7). In contrast, the high pressure limit of eq. (41) leads to

$$\lim_{P\to\infty} \frac{P}{P_0} = \frac{3}{2} .$$

Therefore, our proposal is exact in this limit and also a good approximation for finite pressures.

6. Conclusions

We have presented an exact determination of the direct correlation function of a fluid of aligned planar hard convex orientable bodies using a simple form for the separation of centers at contact. The model has been designed to permit solvability of the thermodynamic and structural properties.

Recently, several authors have considered an approximate proposal for the direct correlation function of an anisotropic fluid in a theoretical attempt concerned with the isotropic–nematic transition of hard ellipsoids [8] and hard ellipses [9]. For the model system considered in this paper we have shown that this approximation underestimates the compressibility factor. This result agrees with the quantitative discrepanceis between theoretical results [8] and computer simulations [23] for a system of hard ellipsoids (see figs. 9 and 10 of ref. [8]). For the hard-ellipse fluid the comparison is a more complicated problem because theory [9] and simulations [24] show different qualitative features. However, we have to bear in mind that other simplifications introduced in these theoretical studies could also be at the origin of the observed discrepancies between theory and computer simulations.

We have also reported an approximate analytical expression for the direct correlation function in terms of a reference direct correlation function of a fluid of spherical molecules. Our proposal leads to the exact equation of state in the high-pressure limit, being moreover a good approximation for finite pressures.

The extension of this new proposal to higher-dimensional systems is planned for a future investigation.

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