

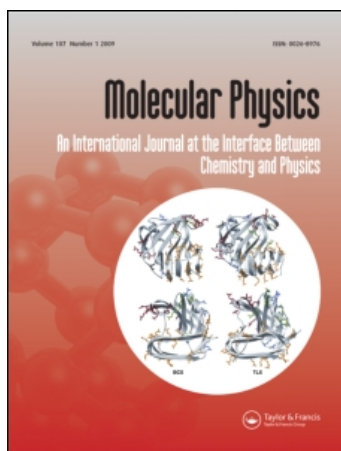
This article was downloaded by:

On: 5 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Molecular Physics

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713395160>

### A perturbation theory of hard quadrupolar fluids

Carlos Vega<sup>a</sup>

<sup>a</sup> Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid, Spain

**To cite this Article** Vega, Carlos(1992) 'A perturbation theory of hard quadrupolar fluids', *Molecular Physics*, 75: 2, 427 – 442

**To link to this Article:** DOI: 10.1080/00268979200100331

**URL:** <http://dx.doi.org/10.1080/00268979200100331>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## A perturbation theory of hard quadrupolar fluids

CARLOS VEGA

Departamento de Química Física, Facultad de Ciencias Químicas,  
Universidad Complutense de Madrid, E-28040 Madrid, Spain

(Received 17 June 1991; accepted 31 July 1991)

A perturbation theory, derived by Boublik, for the polar hard Gaussian overlap model is extended to other hard polar models. The final equations are simple, and good agreement between theory and simulation is found for quadrupolar hard dumbbells and for quadrupolar hard spherocylinders. Since there are no simulation data for quadrupolar hard spherocylinders, we have carried out some Monte Carlo simulations for this system at two different elongations. For quadrupolar hard spheres the theory presented is identical with a previous treatment of Patey and Valleau. Therefore the proposed perturbation theory can be applied to spherical, linear or nonlinear hard quadrupolar fluids, showing good agreement with the simulation results in all the cases.

### 1. Introduction

During the last decade, the statistical mechanics of nonpolar molecular fluids has undergone an important advance. Several perturbation theories have been developed which allow fast determination of the thermodynamic properties of the studied molecular fluid. Good perturbation schemes are now available for the site-site potential model [1-6], for the Gaussian potential model [7, 8] and for the Kihara one [9-12]. Therefore, interest is currently focused on the study of molecular polar fluids which present both short range and long range anisotropic forces. It is clear that the study of fluids with a quadrupolar symmetry charge distribution is simpler than the study of dipolar fluids since the quadrupole-quadrupole interaction decays faster than the dipole-dipole one. Therefore, quadrupolar molecular fluids constitute a good starting point for the study of polar fluids.

The study of quadrupolar fluids is mainly concerned with the change caused in the Helmholtz free energy by the presence of the quadrupole  $A^Q$ . At high densities, the structure of the system is dominated by the repulsive forces. Thus,  $A^Q$  for a purely repulsive system is very close to the value of  $A^Q$  of a system with repulsive and attractive forces as has been shown by simulation. The study of repulsive quadrupolar molecular fluids is therefore worthwhile. Hence it is clear that accurate perturbation theories for hard quadrupolar fluids are needed.

Several studies of hard quadrupolar molecular fluids have recently appeared. Wojcik and Gubbins [13] have studied the hard dumbbell quadrupolar fluid (HDQ) using second order perturbation theory, but the evaluation of the perturbation terms was very complicated and therefore was evaluated from the simulations of the reference system. More recently, Lombardero *et al.* [14] have shown that good results for HDQ can be obtained if the structure of the hard dumbbell fluid is obtained from RAM theory [15, 16]. Although the results are good, they require great numerical effort and, because of this, they are presently of limited utility for calculations covering all the liquid range of the fluid. For the hard Gaussian overlap quadrupolar

model (HGOQ), Boublik [17] has recently proposed a theory which is very simple for numerical calculations. The theory has been tested against simulations of the model [18] and good agreement was found. The goal of the present work is to extend Boublik's theoretical treatment [17, 18] of the HGOQ to other hard polar fluids such as quadrupolar hard dumbbells and quadrupolar hard spherocylinders (HSPQ), and thus to show that a semiquantitative description of the behaviour of these fluids can be achieved with a very simple numerical treatment. This is important, since it allows an improvement in the understanding of the thermodynamic behaviour of quadrupolar linear fluids and in the description of the thermodynamics of real quadrupolar fluids.

Although there are simulation studies of HDQ and HGOQ fluids so that the proposed theory can be tested against the simulation results, the HSPQ has not yet been studied by simulation. We have therefore carried out some simulations for the HSPQ fluid so that the theory can be tested for three very different linear hard quadrupolar models, namely, HDQ, HGOQ and HSPQ. Furthermore, the proposed theory can be applied not only to hard linear quadrupolar fluids but to any hard quadrupolar model.

**2. Perturbation theory of hard linear quadrupolar fluids**

Recently, Boublik has presented a theory for HGO polar fluids [17]. This theory has been checked for HGOQ fluids against simulation results of the model and good agreement has been found [18]. In this section, we shall extend this theoretical approach to other hard quadrupolar fluids. We shall outline the theory briefly, as already been explained in [17] and [18], and show that the theory, originally conceived for the HGO polar fluid, can be extended to any other hard polar fluid.

We shall focus on the quadrupolar fluid, although the extension to dipoles is trivial (see [17]). Let us write the pair potential  $u_{HQ}$  of a hard quadrupolar molecule as

$$u_{HQ}(r, \omega_1, \omega_2) = u_H(r, \omega_1, \omega_2) + \lambda u_Q(r, \omega_1, \omega_2), \tag{1}$$

where  $r$  is the distance between the centres of mass,  $\omega_i$  a set of normalized orientational coordinates for molecule  $i$ ,  $u_H(r, \omega_1, \omega_2)$  the pair potential of the hard system and  $\lambda$  a coupling parameter. The quadrupolar potential  $u_Q$  is given by

$$u_Q = \frac{3Q^2}{4r^5} [1 - 5(c_1^2 + c_2^2) - 15c_1^2c_2^2 + 2(s_1s_2c - 4c_1c_2)^2], \tag{2}$$

where  $Q$  is the quadrupolar moment,  $c_i = \cos \theta_i$ ,  $s_i = \sin \theta_i$  and  $c = \cos(\phi_1 - \phi_2)$ . In equation (2), the polar axis is the one which connects the centres of mass of the molecules. Any hard body potential  $u_H$  can be written as

$$u_H(r, \omega_1, \omega_2) = \infty \quad \text{if } r < d(\omega_1, \omega_2) \tag{3}$$

$$u_H(r, \omega_1, \omega_2) = 0 \quad \text{if } r \geq d(\omega_1, \omega_2) \tag{4}$$

where  $d(\omega_1, \omega_2)$  is the distance between the centres of mass at which the two molecules are in contact with the relative orientation  $\omega_1, \omega_2$  (see figure 1(a)).

Then, expanding the Helmholtz free energy of the system in terms of  $\lambda$ , it appears that [19]

$$A = A_0 + A_1 + A_2 + A_3 + \dots \tag{5}$$

where  $A$  is the Helmholtz free energy of the system interacting through the potential

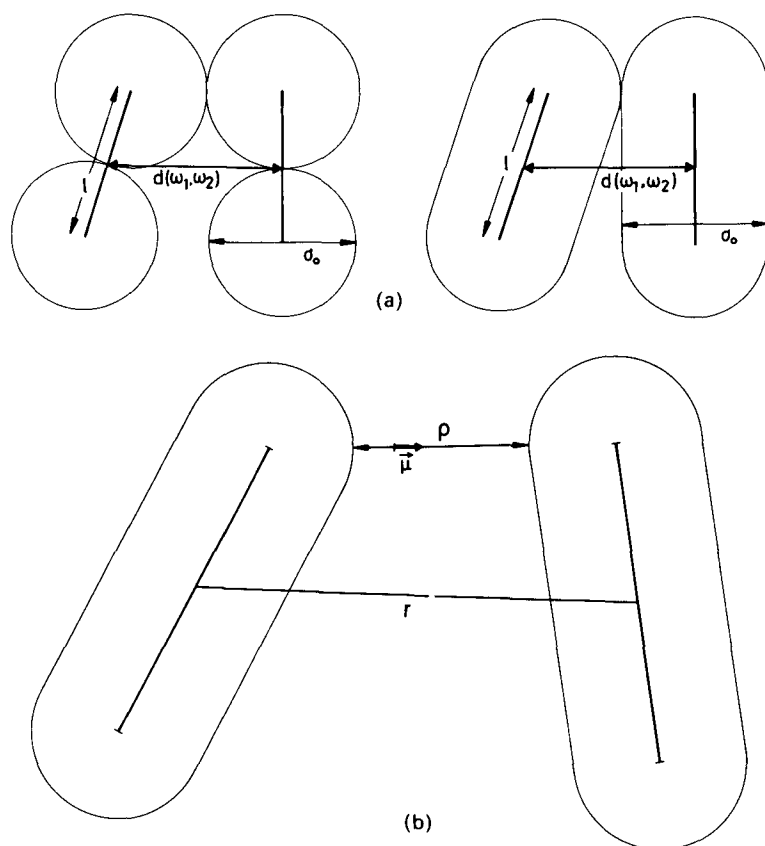


Figure 1. (a) Geometrical meaning of  $d(\omega_1, \omega_2)$  for hard dumbbells and hard spherocylinders. (b) The shortest distance  $\rho$  between hard spherocylinders. We also show the unit vector  $\mu$  in the direction of  $\rho$ .

given by equation (1) with  $\lambda = 1$ ,  $A_0$  is the Helmholtz free energy of the system interacting through equations (3) and (4) (reference system) and the  $A_1, A_2, A_3$  are the first, second and third order perturbation terms, respectively. These perturbation terms are given by integrals involving the perturbation potential and the correlation function of the reference system:

$$A_1 = A_{1A} \tag{6}$$

$$A_2 = A_{2A} + A_{2B} + A_{2C} \tag{7}$$

$$A_3 = A_{3A} + A_{3B} + A_{3C} + A_{3D} + \dots + A_{3N} \tag{8}$$

Explicit formulae for the integrals of equations (6)–(8) can be found in reference [19]. Let us assume, following the treatment in [17] and [18], that it is a good approximation to neglect the contribution from the following perturbation terms:

$$A_{2B} = A_{2C} = A_{3C} = A_{3D} = \dots = A_{3N} = 0 \tag{9}$$

The terms in equation (9) are exactly zero for quadrupolar hard spheres and we assume that they are negligible for other hard quadrupolar models. Therefore the

Helmholtz free energy can be written to third order as

$$A^Q = (A - A_0) = A_{1A} + A_{2A} + A_{3A} + A_{3B}. \quad (10)$$

The terms  $A_{1A}$ ,  $A_{2A}$ ,  $A_{3A}$  and  $A_{3B}$  are given by

$$A_{1A}/NkT = 2\pi n\beta \int \langle g_0(r, \omega_1, \omega_2)u_Q \rangle r^2 dr \quad (11)$$

$$A_{2A}/NkT = -\pi n\beta^2 \int \langle g_0(r, \omega_1, \omega_2)u_Q^2 \rangle r^2 dr \quad (12)$$

$$A_{3A}/NkT = \frac{\pi n\beta^3}{3} \int \langle g_0(r, \omega_1, \omega_2)u_Q^3 \rangle r^2 dr \quad (13)$$

$$A_{3B}/NkT = \frac{n^2\beta^3}{6} \int \langle g_0(1, 2, 3)u_Q(1, 2)u_Q(1, 3)u_Q(2, 3) \rangle dr_{12}dr_{13}, \quad (14)$$

where  $\beta = (kT)^{-1}$ ,  $n$  is the number density,  $g_0(r, \omega_1, \omega_2)$  and  $g_0(1, 2, 3)$  are the pair and the triplet correlation function of the reference system, respectively, with  $i = (r_i, \omega_i)$  and the brackets stand for an unweighted average over all the orientational coordinates. Let us now define

$$Q^{*2} = Q^2/(kT\sigma_0^5) \quad (15)$$

$$X^* = \frac{3Q^{*2}}{4} \quad (16)$$

$$x = r/d(\omega_1, \omega_2) \quad (17)$$

$$d^* = d(\omega_1, \omega_2)/\sigma_0 \quad (18)$$

$$f(\omega_1, \omega_2) = [1 - 5(c_1^2 + c_2^2) - 15c_1^2c_2^2 + 2(s_1s_2c - 4c_1c_2)^2] \quad (19)$$

$$n^* = n\sigma_0^3 \quad (20)$$

$$\eta = nV_m, \quad (21)$$

where  $\sigma_0$  is a characteristic length of the molecule,  $V_m$  is the molecular volume and  $f(\omega_1, \omega_2)$  is the orientational part of  $u_Q$ . Let us now make the following approximation for  $g_0(r, \omega_1, \omega_2)$ :

$$g_0(r, \omega_1, \omega_2, \eta) \cong g(r/d(\omega_1, \omega_2), \eta) \cong g_{HS}(x, \eta) \quad (22)$$

where  $g_{HS}(x, \eta)$  is the radial distribution function of hard spheres at the packing fraction  $\eta$ . Then, substituting equation (22) into equations (11–14) and using the superposition approximation for  $g_0(1, 2, 3)$ , one obtains

$$A_{1A}/NkT = 2\pi n^*X^* \left\langle \frac{f(\omega_1, \omega_2)}{d^{*2}(\omega_1, \omega_2)} \right\rangle \int_1^\infty \frac{g_{HS}(x, \eta)}{x^3} dx \quad (23)$$

$$A_{2A}/NkT = -\pi n^*X^{*2} \left\langle \frac{f^2(\omega_1, \omega_2)}{d^{*7}(\omega_1, \omega_2)} \right\rangle \int_1^\infty \frac{g_{HS}(x, \eta)}{x^8} dx \quad (24)$$

$$A_{3A}/NkT = \frac{\pi n^*X^{*3}}{3} \left\langle \frac{f^3(\omega_1, \omega_2)}{d^{*12}(\omega_1, \omega_2)} \right\rangle \int_1^\infty \frac{g_{HS}(x, \eta)}{x^{13}} dx \quad (25)$$

$$A_{3B} = \gamma \int_\Delta \left\langle \frac{f(1, 2)f(1, 3)f(2, 3)}{d_{12}^{*3}d_{13}^{*3}d_{23}^{*3}} \right\rangle \frac{g_{HS}(x_{12}, \eta)g_{HS}(x_{13}, \eta)g_{HS}(x_{23}, \eta)}{x_{12}^4x_{13}^4x_{23}^4} \times dx_{12}dx_{13}dx_{23} \quad (26)$$

and

$$\gamma = \frac{4\pi^2 n^{*2} X^{*3}}{3} \tag{27}$$

In equations (23–26) the brackets stand for orientational average, but in equation (26) this average has to be calculated while maintaining the shape of the triangle made up by the centres of mass. The symbol  $\Delta$  denotes integration over  $x_{12}, x_{13}, x_{23}$  which form a triangle with a given set of angles  $(\alpha_1, \alpha_2, \alpha_3)$  between the centres of the molecules. Let us now define

$$I(\text{shape}) = \left\langle \frac{f(\omega_1, \omega_2)}{d^{*2}(\omega_1, \omega_2)} \right\rangle \tag{28}$$

$$J(\text{shape}) = \left\langle \frac{f^2(\omega_1, \omega_2)}{d^{*4}(\omega_1, \omega_2)} \right\rangle \tag{29}$$

$$K(\text{shape}) = \left\langle \frac{f^3(\omega_1, \omega_2)}{d^{*6}(\omega_1, \omega_2)} \right\rangle \tag{30}$$

$$M(\text{shape}, \alpha_1, \alpha_2) = \left\langle \frac{f(1, 2)f(1, 3)f(2, 3)}{d_{12}^{*3} d_{13}^{*3} d_{23}^{*3}} \right\rangle \tag{31}$$

$$a(\eta) = \int_1^\infty \frac{g_{HS}(x, \eta)}{x^3} dx \tag{32}$$

$$b(\eta) = \int_1^\infty \frac{g_{HS}(x, \eta)}{x^8} dx \tag{33}$$

$$c(\eta) = \int_1^\infty \frac{g_{HS}(x, \eta)}{x^{13}} dx \tag{34}$$

$$e(\eta, x_{12}, x_{13}, x_{23}) = \frac{g_{HS}(x_{12}, \eta)g_{HS}(x_{13}, \eta)g_{HS}(x_{23}, \eta)}{x_{12}^4 x_{13}^4 x_{23}^4} \tag{35}$$

The dependence of the integrals  $I, J, K, M$  on the molecular shape arises from the fact that  $d(\omega_1, \omega_2)$  is a function of the molecular shape. Equations (23–26) can now be written as

$$A_{1A}/NkT = 2\pi n^* X^* I(\text{shape}) a(\eta) \tag{36}$$

$$A_{2A}/NkT = -\pi n^* X^{*2} J(\text{shape}) b(\eta) \tag{37}$$

$$A_{3A}/NkT = \frac{\pi n^* X^{*3}}{3} K(\text{shape}) c(\eta) \tag{38}$$

$$A_{3B}/NkT = \gamma \int_{\Delta} M(\text{shape}, \alpha_1, \alpha_2) e(\eta, x_{12}, x_{13}, x_{23}) dx_{12} dx_{13} dx_{23} \tag{39}$$

To accelerate the convergence of series (10), a Pade approximant can be used and we then have

$$A^Q = (A - A_0) = A_{1A} + A_{2A}(1 - (A_{3A} + A_{3B})/A_{2A})^{-1} \tag{40}$$

The pressure and internal energy of the hard quadrupolar fluid can be obtained from the expressions:

$$Z = pV/NkT = Z_H + \left( \frac{\partial A_Q/NkT}{\partial \eta} \right)_T \eta \tag{41}$$

$$U/NkT = X^* \left( \frac{\partial A_Q/NkT}{\partial X^*} \right)_n, \tag{42}$$

where  $Z_H$  is the compressibility factor of the hard body fluid.

Equations (10) and (40) are the basic expressions of this section. The proposed perturbation scheme can be applied to any hard quadrupolar fluid. They have already been used in references [17] and [18] for the HGO fluid, but in this work we have extended them to any other hard quadrupolar fluid. The generalization is contained in equation (22).

### 3. Calculations and simulation details

In this work we have studied three different kinds of hard quadrupolar fluids, namely, the quadrupolar hard Gaussian overlap model, the quadrupolar hard dumbbell model and the quadrupolar hard spherocylinder model. The pair potential in these three models is given by equation (1). For the hard Gaussian overlap model  $u_H$  is given by [20]

$$u_H = \infty \quad r < \sigma(\omega_1, \omega_2) \tag{43}$$

$$u_H = 0 \quad r \geq \sigma(\omega_1, \omega_2) \tag{44}$$

$$\left( \frac{\sigma(\omega_1, \omega_2)}{\sigma_0} \right)^2 = \left( 1 - \chi \frac{c_1^2 + c_2^2 + -2\chi c_1 c_2 (c_1 c_2 + s_1 s_2 c)}{1 - \chi (c_1 c_2 + s_1 s_2 c)^2} \right)^{-1}, \tag{45}$$

where  $\sigma_0$  is a width,  $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$  and  $\kappa$  is the length to breadth ratio. For a hard dumbbell (HD),  $u_H$  is given by

$$u_H = \infty \quad \text{if any } r_{ij} < \sigma_0 \text{ } i, j = 1, 2 \tag{46}$$

$$u_H = 0 \quad \text{if all } r_{ij} \geq \sigma_0 \text{ } i, j = 1, 2 \tag{47}$$

where  $r_{ij}$  is the distance between the site  $i$  of molecule 1 and site  $j$  of molecule 2.  $\sigma_0$  is the diameter of the sphere attached to the site. The shape parameter for hard dumbbell is  $L^* = l/\sigma_0$  where  $l$  is the distance between the sites.

For hard spherocylinder (HSP),  $u_H$  is given by

$$u_H = \infty \quad \rho(\omega_1, \omega_2) = 0 \tag{48}$$

$$u_H = 0 \quad \rho(\omega_1, \omega_2) > 0 \tag{49}$$

where  $\rho(\omega_1, \omega_2)$  is the shortest distance between the cores (rods) of the spherocylinder (see figure 1(b)). Algorithms to find the shortest distance between rods  $\rho(\omega_1, \omega_2)$  can be found elsewhere [21, 22]. The characteristic parameter is  $L^* = l/\sigma_0$  where  $l$  is the length of the rod and  $\sigma_0$  is the breadth of the spherocylinder (see figure 1(a)).

To evaluate  $I(\text{shape})$ ,  $J(\text{shape})$  and  $K(\text{shape})$  (equations (28–30)) the function  $d(\omega_1, \omega_2)$  is needed. For the HGO,  $d(\omega_1, \omega_2)$  is given by  $\sigma(\omega_1, \omega_2)$  (see equation (45)). For hard dumbbells it is also very easy to evaluate  $d(\omega_1, \omega_2)$ <sup>23</sup> but for hard spherocylinders it has to be evaluated numerically for every relative orientation. The integrals  $I, J, K$  were evaluated numerically using the Conroy integration method with 10<sup>5</sup> relative orientations, generated by the procedure of reference [24].

In table 1 we give  $I, J$  and  $K$  for several linear models and for several anisotropies. For completeness we have also included the values of  $I, J$  and  $K$  for the HGO fluid. The estimated accuracy in  $I$  is  $1 \times 10^{-4}$ , in  $J$  it is better than 0.5% and in  $K$  it is of the order of 0.5%. The function  $I$  is zero within the numerical uncertainties for the

Table 1. Values of  $I, J$  and  $K$  (see text) for different linear geometries. Hard Gaussian overlap fluid (HGO), hard dumbbell (HD), hard spherocylinder (HSP). We also show the average of  $d^3(\omega_1, \omega_2)$  over all the relative orientations. In the HGO and HSP model,  $\sigma_0$  stands for the breadth of the molecule while, for HD,  $\sigma_0$  is the diameter of the sphere. For  $\kappa = 1$  or  $L^* = 0$  the exact values of  $I, J, K$  are 0, 224/45 and 1024/245, respectively. We show, however, the values obtained numerically also in that case.

$\kappa$	$I$	$J$	$K$	$\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle$
<b>HGO</b>				
1	0.0000	4.9777	4.1792	1.0000
1.2	0.0000	2.8231	0.7910	1.2133
1.35	0.0000	2.0302	0.5132	1.3910
1.50	0.0000	1.5525	0.4792	1.5840
1.65	0.0000	1.2458	0.4770	1.7925
1.80	0.0000	1.0385	0.4716	2.0168
2.00	0.0000	0.8527	0.4562	2.3406
2.2	0.0000	0.7282	0.4361	2.6932
2.5	0.0000	0.6059	0.4052	3.2768
$L^*$	$I$	$J$	$K$	$\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle$
<b>HD</b>				
0	0.0000	4.9777	4.1792	1.0000
0.1	-0.0006	3.3422	1.3521	1.1536
0.2	-0.0025	2.3813	0.5299	1.3139
0.3	-0.0056	1.7859	0.2851	1.4801
0.4	-0.0100	1.4009	0.2132	1.6513
0.50	-0.0157	1.1441	0.1927	1.8265
0.60	-0.0226	0.9700	0.1867	2.0045
0.70	-0.0308	0.8527	0.1836	2.1843
0.80	-0.0403	0.7776	0.1811	2.3648
<b>HSP</b>				
0	0.0000	4.9777	4.1792	1.0000
0.1	-0.0006	3.3305	1.3454	1.1554
0.2	-0.0023	2.3694	0.5306	1.3168
0.3	-0.0050	1.7693	0.2922	1.4857
0.4	-0.0082	1.3763	0.2268	1.6621
0.5	-0.0117	1.1083	0.2130	1.8460
0.6	-0.0151	0.9190	0.2128	2.0374
0.7	-0.0182	0.7810	0.2149	2.2363
0.8118	-0.0211	0.6671	0.2168	2.4675
0.9	-0.0230	0.5982	0.2174	2.6566
1	-0.0247	0.5360	0.2171	2.8780

HGO fluid, and it is small but different from zero for the HD and the HSP fluids. This is in agreement with the values of the  $A_{1A}$  term from simulations for the HGOQ [18] and for the HDQ [13] fluids. For  $\kappa = 1$  (HGO) or  $L^* = 0$  (HD and HSP), the hard body reduces to a hard sphere. For hard spheres,  $I, J, K$  can be obtained analytically. Their exact values [25] are  $I = 0, J = 224/45 = 4.9778, K = 1024/245 = 4.1796$ , which compare well with the values obtained numerically  $I = 0.0000, J = 4.9777, K = 4.1792$  and presented in table 1. We have fitted  $I, J, K$  and  $\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle$  as a function of the molecular anisotropy to empirical formulae for the HGO, HD and HSP models. The fitting expressions are given in the appendix and allow us to apply the theory to anisotropies differing from those presented in table 1.



The evaluation of the function  $M(\text{shape}, \alpha_1, \alpha_2)$  of equation (31) is numerically difficult. It is analytical for hard spheres but not for other geometries. For hard spheres it is given by [25]

$$M(\text{sphere}, \alpha_1, \alpha_2) = 1/450 \{ -27 + 220 \cos \alpha_1 \cos \alpha_2 \cos \alpha_3 + 490 \cos 2\alpha_1 \cos 2\alpha_2 \cos 2\alpha_3 + 175 [\cos 2(\alpha_1 - \alpha_2) + \cos 2(\alpha_1 - \alpha_3) + \cos 2(\alpha_2 - \alpha_3)] \} \quad (50)$$

Following the procedure of [18], we shall obtain an estimate of the  $A_{3B}$  term for nonspherical models from the value of  $A_{3B}$  of a corresponding hard sphere of the same volume at the same packing fraction. The final expression is

$$A_{3B}/NkT = \gamma/F^5 \int_{\Delta} M(\text{sphere}, \alpha_1, \alpha_2) e(\eta, x_{12}, x_{13}, x_{23}) dx_{12} dx_{13} dx_{23} \quad (51)$$

$$F = (V_m/\sigma_0^3)/(\pi/6) \quad (52)$$

$$z(\eta) = \int_{\Delta} M(\text{sphere}, \alpha_1, \alpha_2) e(\eta, x_{12}, x_{13}, x_{23}) dx_{12} dx_{13} dx_{23} \quad (53)$$

The evaluation of  $a(\eta)$ ,  $b(\eta)$ ,  $c(\eta)$  of equations (32–34) and of  $z(\eta)$  of equation (53) has been performed using Verlet–Weiss parametrization [26] of  $g_{HS}(r/d)$  and Simpson's integration rule. We have fitted them to empirical expressions which are given in the appendix.

To obtain the pressure of the hard quadrupolar fluid it is necessary to use an equation of state EOS ( $Z_H$ ) of the hard body (see equation (41)). For HGO, several EOS have been proposed recently [27, 28]. For HSP we shall use [29, 30]

$$Z_H = \frac{1 + (3\alpha - 2)\eta + (3\alpha^2 - 3\alpha + 1)\eta^2 - \alpha(6\alpha - 5)\eta^3}{(1 - \eta)^3} \text{HSP} \quad (54)$$

$$\alpha = (2 + L^*)(1 + L^*)/(3L^* + 2) \text{HSP} \quad (55)$$

and for HD we shall use [30, 31]

$$Z_H = \frac{1 + (3\alpha - 2)\eta + (3\alpha^2 - 3\alpha + 1)\eta^2 - \alpha^2\eta^3}{(1 - \eta)^3} \text{HD} \quad (56)$$

$$\alpha = (2 + L^*)(1 + L^*)/(3L^* + 2 - L^{*3}) \text{HD} \quad (57)$$

Thermodynamic integration of equations (54–57) allows us to determine the free energy  $A_0$  of the hard body (see equations (10) and (40)).

The HGOQ fluid and the HDQ have been studied by simulation [13, 14, 18]. The proposed perturbation scheme can therefore be tested against simulation data. However, there are no simulation data of the HSPQ fluid. We have carried out some MC runs for this model. The main characteristics of the simulations are similar to the ones described in [18] and [32].

We used the standard procedure of Metropolis *et al.* [33]. In all the simulations we used 256 particles in a cubic box with periodic boundary conditions. We started all the runs from an  $\alpha N_2$  FCC lattice. A run consists of an initial period of 3000–5000 trial moves per particle to reach equilibrium followed by a period of 6000–10 000 trial moves per particle to obtain the averages. Every trial move consists of an attempt to change the position of the centre of mass and the orientation of the molecule. The acceptance ratio was kept in the range 25–55%. An order parameter [34] was evaluated

Table 2. MC results obtained for HSPQ fluid.  $Q^{*2} = Q^2/(kT\sigma_0^5)$ .

Model	$L^*$	$n^*$	$Q^{*2}$	$U/NkT$	$Z$
HSPQ	0.3	0.55	0	0	8.04
HSPQ	0.3	0.55	0.277	-0.084	7.99
HSPQ	0.3	0.55	0.555	-0.323	7.62
HSPQ	0.3	0.55	1.111	-1.166	6.90
HSPQ	0.3	0.55	1.666	-2.350	5.75
HSPQ	0.8118	0.36	0	0	8.69
HSPQ	0.8118	0.36	0.454	-0.074	8.68
HSPQ	0.8118	0.36	0.909	-0.260	8.47
HSPQ	0.8118	0.36	1.818	-0.846	7.79
HSPQ	0.8118	0.36	2.727	-1.688	6.98

during the runs to be sure that the system was orientationally equilibrated. We neglect the contribution of the quadrupole to the long range correction. Similar treatment has been used in references [13, 14, 18, 35]. The quadrupole interaction was cut at a distance of  $B/2 - l$  where  $B$  is the length of the side of the box.

The internal energy and pressure of the HSPQ fluid were obtained from

$$U = U^Q \tag{58}$$

$$U^Q = \sum_{i < j} u_Q(i, j) \tag{59}$$

$$Z = 1 + 2/3\pi n g_{av}(\rho = 0) \langle r \cdot \mu \rangle_{\rho=0} + Z^Q \tag{60}$$

$$Z^Q = \frac{\rho^Q V}{NkT} = \frac{5U^Q}{3NkT}, \tag{61}$$

where  $g_{av}(\rho)$  is the surface to surface distribution function [30] and the meaning of  $\mu$  is illustrated in figure 1(b). The values at contact are obtained by extrapolation to  $\rho = 0$  of the corresponding functions.

$A_Q$  was obtained from the simulations by using the squared quadrupole as the coupling parameter within Kirkwood's formalism [36]

$$A^Q = A(Q = Q) - A(Q = 0) = \int_0^{Q^2} \langle U^Q/Q^2 \rangle dQ^2. \tag{62}$$

We followed the procedure of Patey *et al.* [25] and fitted the MC values of  $U^Q/NkT$  to the expression

$$U^Q/NkT = \frac{tQ^{*4}(sQ^{*2} + 2)}{(1 + sQ^{*2})^2} \tag{63}$$

so that the parameters  $t$  and  $s$  have to be determined. Substituting equation (63) in equation (62) one gets

$$A^Q/NkT = \frac{tQ^{*4}}{(1 + sQ^{*2})}. \tag{64}$$

We have studied the system  $L^* = 0.3$  at the state point  $n^* = 0.55$  with values of  $Q^{*2}$  from 0 to 1.666 and the system  $L^* = 0.8118$  at the state point  $n^* = 0.36$  with values of  $Q^{*2}$  from 0 to 2.727. Table 2 shows the MC results. In table 3 we show the values of  $t$  and  $s$  so that  $A_Q$  can be determined (see equation (64)).

Table 3. Coefficients  $t$  and  $s$  in equations (63) and (64) obtained from the MC data of table 2.

Model	$L^*$	$n^*$	$t$	$s$
HSPQ	0.30	0.55	-0.5921	0.1542
HSPQ	0.8118	0.36	-0.1921	0.1599

4. Results and discussion

It was proved that the perturbation scheme of section 2 gives satisfactory results for the HGOQ fluid. In this section we shall show that the extension of the theory to HDQ and HSPQ outlined in section 2 is able to describe the thermodynamic behaviour of these fluids.

Table 4 shows a comparison between  $A^Q$ , the compressibility factor and internal energy for HDQ, as obtained from MC and from the theory of this work. We also show the results from Lombardero *et al.* [14], who used a RAM theory to get the structure of the hard dumbbell fluid. For  $A^Q$  and  $Z$ , equation (40) works much better than equation (10) but, for the internal energy, equation (10) seems to be superior.  $A^Q$ ,  $Z$  and  $U$  obtained from equation (40) are smaller than those obtained from equation (10). Equation (40) is able to describe  $A^Q$  and  $Z$  very well until high values of the quadrupole, such as  $X^* = 2.5$ . For the highest value of the quadrupole,  $X^* = 3$ , equation (40) fails. Equation (10) yields good agreement for internal energy for all the values of the quadrupole. The results of the Padé approximant (equation (40)) are comparable with those obtained from RAM theory. This holds for  $A^Q$ ,  $Z$  and  $U$ . This is important because the perturbation theory proposed in this work proves to be computationally less demanding than the RAM theory.

Table 4.  $A^Q$ ,  $Z$  and  $U$  for quadrupolar hard dumbbells as obtained from MC [14], from RAM theory [14] and from the proposed perturbation scheme of this work. The elongation is  $L^* = 0.60$  and the density  $n^* = 0.4263$ .

$X^*$	MC [14]	Eqn (10)	Eqn (40)	RAM [14]
$A^Q/NkT$				
0.5	-0.15	-0.12	-0.12	-0.15
1.0	-0.48	-0.42	-0.43	-0.50
1.5	-0.96	-0.89	-0.90	-1.00
2.0	-1.57	-1.49	-1.52	-1.66
2.5	-2.29	-2.21	-2.28	-2.42
3.00	-3.10	-3.02	-3.16	-3.29
$Z$				
0.5	7.92	7.93	7.93	7.82
1.0	7.24	7.48	7.41	7.25
1.5	6.49	6.86	6.62	6.50
2.0	5.51	6.21	5.60	5.61
2.5	4.37	5.61	4.37	4.63
3.0	3.44	5.17	2.98	3.59
$U/NkT$				
0.5	-0.24	-0.22	-0.22	-0.255
1.0	-0.82	-0.77	-0.78	-0.867
1.5	-1.66	-1.61	-1.65	-1.751
2.0	-2.64	-2.66	-2.77	-2.844
2.5	-3.86	-3.85	-4.12	-4.100
3.0	-5.09	-5.11	-5.66	-5.484

Table 5.  $A^Q$ ,  $Z$  and  $U$  for quadrupolar hard spherocylinder with  $L^* = 0.8118$  and  $n^* = 0.36$  as obtained from MC and from the proposed perturbation scheme of this work.

$Q^{*2}$	MC	Eqn (10)	Eqn (40)
$A^Q/NkT$			
0.454	-0.04	-0.04	-0.04
0.909	-0.14	-0.13	-0.13
1.818	-0.49	-0.45	-0.46
2.727	-0.99	-0.92	-0.95
$Z$			
0	8.69	8.67	8.67
0.454	8.68	8.61	8.61
0.909	8.47	8.45	8.45
1.818	7.79	7.94	7.88
2.727	6.98	7.26	7.04
$U/NkT$			
0.454	-0.074	-0.066	-0.066
0.909	-0.260	-0.232	-0.234
1.818	-0.846	-0.799	-0.823
2.727	-1.688	-1.577	-1.687

In table 5 we show the results for HSPQ at  $L^* = 0.8118$ . The agreement between MC and theoretical results is again very good. Also, the Padé approximant (40) works better than equation (10) at high values of the quadrupole moment, where there are appreciable differences between the two methods. This holds for  $A^Q$ ,  $Z$  and  $U$ . The quality of the results is very good, taking into account that the anisotropy of the model is rather high and corresponds to a CO<sub>2</sub> like elongation. The density studied corresponds to a packing fraction of about  $\eta = 0.418$ , which is a typical liquid density. The values of  $Q^{*2}$  for CO<sub>2</sub> are ranged from 2.5 (critical temperature) to 3.4 (triple point temperature), so that the results of table 5 can be considered as promising. We have investigated the effect of the quadrupole on the structure for the HSPQ with  $L^* = 0.8118$ . In figure 2 the surface to surface distribution function [30]  $g_{av}(\rho)$  as obtained from MC simulations for a hard spherocylinder and for a hard spherocylinder plus quadrupole is shown. At large and medium distances, the effect of the quadrupole is small. At short distances the presence of the quadrupole increases the value at contact of  $g_{av}(\rho)$ . This accords with the fact that the contact values of the radial distribution function of quadrupolar hard spheres are larger than those of hard spheres. Let us recall that, for hard spheres,  $g_{av}(\rho)$  reduces to the radial distribution function. However, the effect of the quadrupole on  $g_{av}(\rho)$  seems to be less pronounced for hard spherocylinders than for hard spheres. In figure 3 we show the first coefficients  $g_{llm}(r)$  of the expansion of  $g(r, \omega_1, \omega_2)$  in spherical harmonics  $Y_{lm}(\omega)$

$$g(r, \omega_1, \omega_2) = 4\pi \sum_{llm} g_{llm}(r) Y_{lm}(\omega_1) Y_{l-m}(\omega_2) \tag{65}$$

for hard spherocylinders with  $L^* = 0.8118$  when  $Q^{*2} = 0$  and  $Q^{*2} = 2.727$ . The presence of the quadrupole strongly modifies the radial distribution function ( $g_{000}(r)$ ) and the  $g_{200}(r)$  coefficient. The changes are similar to those found for hard dumbbells with quadrupole [13].

In table 6 we show the results for HSPQ with  $L^* = 0.30$ . For the pressure, equation (40) works better than equation (10). However, for  $A^Q$  and  $U$ , equation (10) works slightly better than equation (40). The agreement is again good.

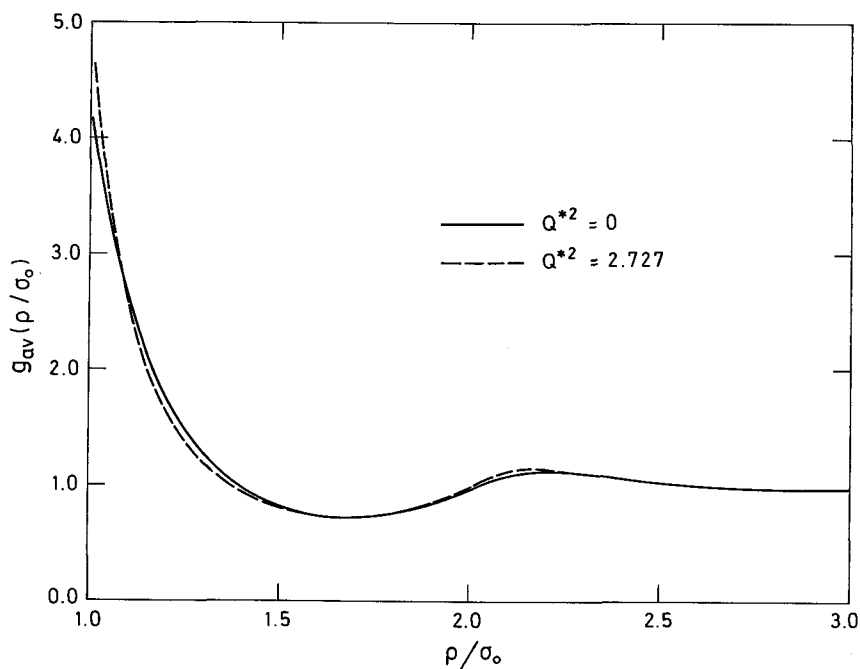


Figure 2. The surface to surface distribution function [30]  $g_{av}(\rho)$  for hard spherocylinders with  $L^* = 0.8118$  and  $n^* = 0.36$ .  $Q^{*2} = 0$  (solid line) and  $Q^{*2} = 2.727$  (dashed line).

Table 6.  $A^Q$ ,  $Z$  and  $U$  for quadrupolar hard spherocylinder with  $L^* = 0.30$  as obtained from MC and from the proposed perturbation scheme of this work.

$Q^{*2}$	MC	Eqn (10)	Eqn (40)
$A^Q/NkT$			
0.277	-0.04	-0.04	-0.04
0.555	-0.17	-0.17	-0.17
1.110	-0.62	-0.65	-0.65
1.666	-1.31	-1.39	-1.41
$Z$			
0.00	8.04	7.89	7.89
0.277	7.99	7.81	7.81
0.555	7.62	7.61	7.59
1.110	6.90	6.96	6.76
1.666	5.75	6.21	5.51
$Q^*$	MC	Eqn (10)	Eqn (40)
$U/NkT$			
0.277	-0.084	-0.086	-0.086
0.555	-0.323	-0.323	-0.330
1.110	-1.166	-1.226	-1.243
1.666	-2.350	-2.562	-2.642

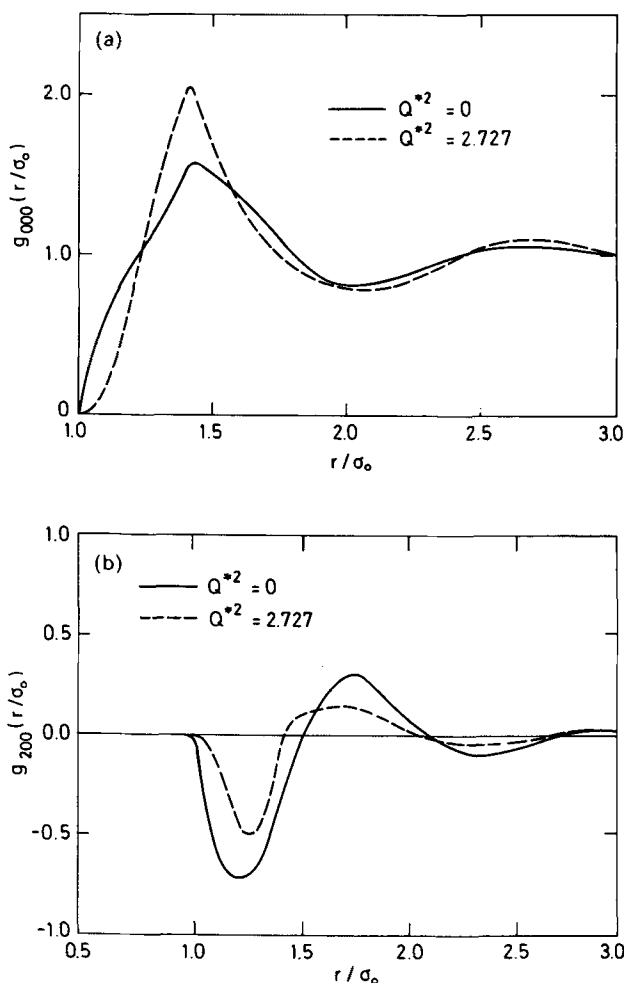


Figure 3. Coefficients of the expansion in spherical harmonics of the pair correlation function for hard spherocylinders with  $L^* = 0.8118$  and  $n^* = 0.36$ .  $Q^{*2} = 0$  (solid line) and  $Q^{*2} = 2.727$  (dashed line): (a) radial distribution function which is given by the  $g_{000}(r)$  coefficient; (b)  $g_{200}(r)$  coefficient.

Let us remark that in all cases the values of  $A_{2A}$  were negative while those of  $A_{3A}$  and  $A_{3B}$  were positive. That guarantees that the second term of equation (40) remain finite. The ratio  $A_{3A}/A_{3B}$  is not much affected by the value of the quadrupole for a given geometry at a fixed density. However, this ratio depends strongly on the geometry, ranging from large values in the case of very anisotropic models to values slightly smaller than unity for spherical or quasispherical models. To neglect the  $A_{3B}$  term provokes a decrease of  $A^Q$ , and this conclusion holds for equation (10) and for the Padé approximant (40). The values of  $A^Q$  obtained from equation (40) are always smaller than those from equation (10) as follows from the different sign of the  $A_2$  and the  $A_3$  ( $A_{3A}$  and  $A_{3B}$ ) perturbation terms.

Until now we have shown results for anisotropic quadrupolar models. If we set  $L^* = 0$  then we get results for quadrupolar hard spheres. To illustrate the quality of the results we show in table 7  $A^Q$ ,  $Z$  and  $U$  for quadrupolar hard spheres. For  $Z$  and

Table 7.  $A^Q$ ,  $Z$  and  $U$  for quadrupolar hard spherocylinder with  $L^* = 0.8344$  as obtained from MC and from the proposed perturbation scheme of this work.

$Q^{*2}$	MC [25]	Eqn (10)	Eqn (40)
$A^Q/NkT$			
0.2	-0.09	-0.09	-0.09
0.5882	-0.71	-0.71	-0.73
0.8333	-1.33	-1.29	-1.38
1.25	-2.70	-2.40	-2.81
1.666	-4.32	-3.37	-4.58
$Z$			
0.2	8.77		8.48
0.5882	7.55		7.41
0.8333	6.79		6.40
1.25	4.89		4.30
1.666	2.86		1.90
$U/NkT$			
0.2	-0.18		-0.18
0.5882	-1.30		-1.35
0.8333	-2.33		-2.47
1.25	-4.57		-4.84
1.666	-6.99		-7.60

$U$  we show the results of the Padé approximant (equation (40)) only because equation (10) fails completely in that case. The agreement between MC results and those of equation (40) is again good. This is not surprising since when  $L^* = 0$  the theoretical treatment presented in this work can be reduced to the treatment given by Patey *et al.* [25] of quadrupolar hard spheres. Therefore, the proposed perturbation approach gives good results for spherical and highly nonspherical hard quadrupolar molecules, and can be considered as a natural extension of the theoretical treatment of Patey *et al.* to hard nonspherical quadrupolar systems.

## 5. Conclusion

We have shown how the perturbation scheme proposed by Boublik [17, 18] for the HGOQ can be extended to other hard quadrupolar fluids as HDQ and HSPQ with good results, given the simplicity of the treatment. The extension to dipolar fluids is trivial [17]. The theory developed in section 2 can also be applied to any hard polar fluid. The only numerical problem is the evaluation of the contact diameter  $d(\omega_1, \omega_2)$  for every relative orientation and for every molecular geometry. We have shown that, with a very simple theoretical treatment, it is possible to describe the main features of the contribution of the quadrupole to the Helmholtz free energy, to the pressure and to the internal energy in a hard quadrupolar fluid. Overall, the quality of the results can be considered as good. The main advantage of the formalism is to combine reasonable accuracy with a very high simple numerical treatment.

This work has been financially supported by Project PB 88/0143 of the Spanish DGICYT (Dirección General de Investigación Científica y Técnica). Helpful discussions with Dr S. Lago, Professor T. Boublik and Professor K. E. Gubbins are gratefully acknowledged.

### References

- [1] TILDESLEY, D., 1980, *Molec. Phys.*, **41**, 341.
- [2] LOMBARDEO, M., ABASCAL, J. L. F., and LAGO, S., 1981, *Molec. Phys.*, **42**, 999.
- [3] MCGUIGAN, D. B., LUPKOWSKI, M., PAQUET, D. M., and MONSON, P. A., 1989, *Molec. Phys.*, **67**, 33.
- [4] KOHLER, F., QUIRKE, N., and PERRAM, J., 1979, *J. chem. Phys.*, **71**, 4128.
- [5] FISCHER, J., 1980, *J. chem. Phys.*, **72**, 5371.
- [6] FISCHER, J., LAGO, S., 1983, *J. chem. Phys.*, **78**, 5750.
- [7] BOUBLIK, T., 1989, *Molec. Phys.*, **67**, 1327.
- [8] SEDIWAN, W. B., GUPTA, S., and MCLAUGHLIN, E., 1987, *Molec. Phys.*, **62**, 141.
- [9] BOUBLIK, T., 1987, *J. chem. Phys.*, **87**, 1751.
- [10] PADILLA, P., and LAGO, S., 1989, *Fluid Phase Equilibria*, **48**, 53.
- [11] VEGA, C., and LAGO, S., 1991, *Molec. Phys.*, **72**, 215.
- [12] VEGA, C., and LAGO, S., 1991, *J. chem. Phys.*, **94**, 310.
- [13] WOJCIK, M. C., and GUBBINS, K. E., 1984, *J. phys. Chem.*, **88**, 6559.
- [14] LOMBARDEO, M., MARTIN, C., LOMBA, E., and ABASCAL, J. L. F., 1989, *J. phys. Chem.*, **93**, 4636.
- [15] SMITH, W. R., and NEZBEDA, I., 1983, *ACS Adv. Chem. Ser.*, **204**, 235.
- [16] SMITH, W. R., and NEZBEDA, I., 1981, *Molec. Phys.*, **44**, 347.
- [17] BOUBLIK, T., 1990, *Molec. Phys.*, **69**, 497.
- [18] BOUBLIK, T., VEGA, C., LAGO, S., and DIAZ-PEÑA, M., 1990, *Molec. Phys.*, **71**, 1193.
- [19] GRAY, C. G., and GUBBINS, K. E., 1984, *Theory of Molecular Fluids*, Vol. I (Clarendon Press).
- [20] BHETHANABOTLA, W. R., and STEELE, W. A., 1987, *Molec. Phys.*, **60**, 249.
- [21] SEVILLA, P., and LAGO, S., 1985, *Comput. Chem.*, **9**, 39.
- [22] LAGO, S., and VEGA, C., 1988, *Comput. Chem.*, **12**, 343.
- [23] LABIK, S., SMITH, W. R., POSPISIL, R., and MALIJEVSKY, A., 1990, *Molec. Phys.*, **69**, 649.
- [24] NEZBEDA, I., KOLAFKA, J., and LABIK, S., 1989, *Czech. J. Phys.*, **B**, **39**, 65.
- [25] PATEY, G. N., and VALLEAU, J. P., 1976, *J. chem. Phys.*, **64**, 170.
- [26] VERLET, L., and WEIS, J. J., 1972, *Phys. Rev. A*, **5**, 939.
- [27] RIGBY, M., 1989, *Molec. Phys.*, **68**, 687.
- [28] BOUBLIK, T., and DIAZ-PEÑA, M., 1990, *Molec. Phys.*, **70**, 1115.
- [29] BOUBLIK, T., 1981, *Molec. Phys.*, **42**, 209.
- [30] BOUBLIK, T., and NEZBEDA, I., 1986, *Coll. Czech. chem. Commun.*, **51**, 2301.
- [31] BOUBLIK, T., 1975, *J. chem. Phys.*, **63**, 4084.
- [32] VEGA, C., and FRENKEL, D., 1989, *Molec. Phys.*, **67**, 633.
- [33] METROPOLIS, N., ROSENBLUTH, A. W., ROSENBLUTH, M. N., TELLER, A. H., and TELLER, E., 1953, *J. chem. Phys.*, **21**, 1087.
- [34] EPPENGA, R. E., and FRENKEL, D., 1984, *Molec. Phys.*, **52**, 1303.
- [35] BOHN, M., FISCHER, J., and HAILE, J., 1988, *Molec. Phys.*, **65**, 797.
- [36] KIRKWOOD, J. G., 1935, *J. chem. Phys.*, **3**, 300.
- [37] CUESTA, J. A., and TEJERO, C. F., 1991, *Phys. Lett. A*, **152**, 15.

### Appendix

The functions  $a(\eta)$ ,  $b(\eta)$ ,  $c(\eta)$  and  $z(\eta)$  (equations (32), (33), (34) and (53), respectively, have been evaluated by using the Verlet–Weis parametrization of  $g_{HS}(r/d)$  and Simpson's integration rule. We have fitted  $a(\eta)$ ,  $b(\eta)$ ,  $c(\eta)$ ,  $z(\eta)$  to the empirical expressions

$$a(\eta) = 0.49204 + 0.50876\eta^2 + 0.12026\eta^2 \quad (\text{A1})$$

$$b(\eta) = 0.14154 \exp(2.00393\eta) \quad (\text{A2})$$

$$c(\eta) = 0.08283 + 0.19477\eta + 0.10865\eta^2 + 0.63337\eta^3 \quad (\text{A3})$$

$$z(\eta) = 0.01555 \exp(4.3158\eta) \quad (\text{A4})$$

We have also fitted the function  $I(\text{shape})$ ,  $J(\text{shape})$ ,  $K(\text{shape})$  and  $\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle$



from table 1 for the HGO, HD and HSP fluid to empirical expressions. That allows the interpolation the values of  $I, J, K$  and  $\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle$  to anisotropies not included in table 1. In the case of the HGO model, the function  $\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle$  can be obtained analytically [37] and is given in equation (A8), where  $\chi$  stands for  $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$ .

*HGO*

$$I(\kappa) = 0 \tag{A5}$$

$$J(\kappa) = 150.976 - 449.321\kappa + 576.401\kappa^2 - 400.301\kappa^3 + 157.387\kappa^4 - 33.0521\kappa^5 + 2.88737\kappa^6 \tag{A6}$$

$$K(\kappa) = \exp(104.879 - 278.632\kappa + 291.025\kappa^2 - 150.42\kappa^3 + 38.48\kappa^4 - 3.90058\kappa^5) \tag{A7}$$

$$\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle = \kappa/2 \left( 1 + \frac{\arcsin(\chi)}{\chi(1 - \chi^2)^{1/2}} \right) \tag{A8}$$

*HD*

$$I(L^*) = -5.45473 \times 10^{-6} + 3.25328 \times 10^{-4}L^* - 6.33442 \times 10^{-2}L^{*2} \tag{A9}$$

$$J(L^*) = 4.97695 - 20.9293L^* + 53.9763L^{*2} - 85.5252L^{*3} + 74.6615L^{*4} - 26.8366L^{*5} \tag{A10}$$

$$K(L^*) = \exp(1.43041 - 11.2838L^* - 6.9547L^{*2} + 79.9358L^{*3} - 118.363L^{*4} + 54.6096L^{*5}) \tag{A11}$$

$$\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle = 1.00007 + 1.49591L^* + 0.399339L^{*2} - 0.170959L^{*3} \tag{A12}$$

*HSP*

$$I(L^*) = -5.91503 \times 10^{-6} + 3.25087 \times 10^{-3}L^* - 9.11933 \times 10^{-2}L^{*2} + 8.80672 \times 10^{-2}L^{*3} - 2.48054 \times 10^{-2}L^{*4} \tag{A13}$$

$$J(L^*) = 4.97403 - 20.6841L^* + 50.4076L^{*2} - 71.9131L^{*3} + 54.1431L^{*4} - 16.3942L^{*5} \tag{A14}$$

$$K(L^*) = \exp(1.4317 - 11.0522L^* - 12.5528L^{*2} + 117.028L^{*3} - 213.022L^{*4} + 162.835L^{*5} - 46.1821L^{*6}) \tag{A15}$$

$$\langle d^3(\omega_1, \omega_2)/\sigma_0^3 \rangle = 1.00063 + 1.5048L^* + 0.372372L^{*2}. \tag{A16}$$

Equations (A1–A16) along with the proposed perturbation theory allow the determination of the thermodynamic properties of hard quadrupolar fluids.