

Quadrupolar hard Gaussian-overlap fluid

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Monte Carlo simulations are performed for a system of hard Gaussian-overlap molecules with embedded permanent quadrupole moment. Two shapes of the hard bodies are considered, with characteristic parameter $\kappa = 1.792$ and 2.2 and three values of the quadrupole moment. The results obtained for the residual internal energy, Helmholtz function and compressibility factor at three densities for $\kappa = 1.792$ and one density for $\kappa = 2.2$ are used to test the recently proposed perturbation theory of polar non-spherical-molecule fluids.

1. Introduction

Description of the equilibrium behaviour of pure fluids and their mixtures is of great importance both for theoretical and chemical engineering practice. Following progress in the understanding and description of the behaviour of non-polar fluids composed of molecules of spherical or non-spherical shape [1-3] and fluids of spherical molecules with different electrostatic interactions [4, 5], current interest is focused upon studies of systems of non-spherical polar molecules [4, 6, 7]. The non-spherical shape of molecules has usually been modelled by a two-centre interaction-site potential, such as, for example, hard dumbbells, and dipolar or quadrupolar moments have been considered. Simulations in pure fluids and mixtures of quadrupolar molecules, differing in shape [8], have yielded basic pseudo-experimental data on structure and thermodynamic functions. Perturbation theories (of non-spherical molecules), based either on spherical or non-spherical reference systems, however, have not proved satisfactory [8], and their extensions to models with more interaction sites or nonlinear shapes is difficult.

For non-polar fluids convex-molecule perturbation theory has proved [2, 9] to be accurate and simple in application. Inclusion of electrostatic interactions, however, has encountered the problem of the different (central) character of electrostatic interactions in comparison with the non-central character of the Kihara-like potential. To overcome this difficulty, we recently proposed for fluids of ellipsoidal molecules a version of perturbation theory in which the contribution of electrostatic interactions is evaluated via that of a hard Gaussian-overlap (HGO) model with embedded permanent multipole moment(s) [10]. In the absence of any pseudo-experimental data for fluids of convex molecules with electrostatic interactions, the theory was applied to characterize the behaviour of quadrupolar hard dumbbells [6]. A fair prediction of thermodynamic functions of this system was obtained. However, in order to subject the theory to a severe test, pseudo-experimental data on the HGO fluid with electrostatic interactions are desired. To this end, we have performed Monte

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Carlo (MC) simulations in the quadrupolar HGO fluid (HGOQ). The shape parameter κ (which corresponds to the length-to-breadth ratio of hard ellipsoids of revolution (HER)) and values of the reduced quadrupole moment Q were chosen in such a way that they correspond to the values of the previously studied fluid of quadrupolar hard dumbbells [6, 7]. Three values of the packing fraction were chosen, covering the important density region. In addition to this, the HGOQ fluid with $\kappa = 2.2$ was studied at one density. The previously proposed perturbation theory of HGOQ systems was applied to predict thermodynamic functions, the residual internal energy, Helmholtz function and the compressibility factor of the studied systems, and an attempt was made to estimate the previously neglected part of the third-order term.

2. Theory

In the recently proposed perturbation theory [10] of polar hard Gaussian-overlap fluids (characterized by the shape parameter κ [11]) the pair potential is given by a sum of two terms

$$u(r\omega_1\omega_2) = u_{\text{HGO}}(r\omega_1\omega_2) + u_Q(r\omega_1\omega_2), \tag{1}$$

where the HGO pair potential [12] is

$$u_{\text{HGO}}(r\omega_1\omega_2) = \begin{cases} r < \sigma(\omega_1\omega_2), \\ r > \sigma(\omega_1\omega_2), \end{cases}$$

with

$$\left(\frac{\sigma}{\sigma_0}\right)^2 = \left(1 - \chi \frac{\cos^2 \theta_1 + \cos^2 \theta_2 - 2\chi \cos \theta_1 \cos \theta_2 \cos \phi_{12}}{1 - \chi^2 \cos^2 \phi_{12}}\right)^{-1}, \tag{2}$$

where σ_0 is a ‘width’, r is the centre-to-centre distance, ω_i represents the orientational coordinates (θ_i, ϕ_i) and $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$. The only electrostatic interaction considered here is that of permanent quadrupolar moments Q ; for u_Q [4]

$$u_Q(r\omega_1\omega_2) = \frac{3Q^2}{4r^5} [1 - 5(\cos^2 \theta_1 + \cos^2 \theta_2 + 3 \cos^2 \theta_1 \cos^2 \theta_2) + 2(\sin \theta_1 \sin \theta_2 \cos \phi_{12} - 4 \cos \theta_1 \cos \theta_2)^2]. \tag{3}$$

The basis of the method [10, 13], which stems from the results of the study of Kabadi and Steele [14], is the assumption made regarding the molecular distribution function $g^0(r\omega_1\omega_2)$, of an HGO fluid, i.e.

$$g^0(r\omega_1\omega_2) = g^{\text{av}}(x) = g^{\text{hs}}(x) \tag{4}$$

where

$$g^{\text{av}}(x) = \int g(x\omega_1\omega_2) \left(\frac{\sigma}{\sigma_0}\right)^3 d\omega_1 d\omega_2 / \int \left(\frac{\sigma}{\sigma_0}\right)^3 d\omega_1 d\omega_2. \tag{5}$$

Here $x = r/\sigma$, and g^{hs} is the radial distribution function of hard spheres, taken at the same packing fraction η as that of the HGO fluid. Within the above approximation, the first-order term in the perturbation expansion of the Helmholtz function $A - A^{\text{HGO}}$, (due to the quadrupolar moment) vanishes (as found by numerical integration for $\kappa = 1-2.5$ and conjectured from the behaviour at $\kappa = 1$ and the general dependence of the J, K, \dots integrals on κ). The second-order term is [10]

$$\frac{A_2}{NkT} = -\pi\rho^* X^{*2} J(\kappa) \int_1^\infty g^{\text{hs}}(x) x^{-2n+2} dx, \tag{6}$$

where $\rho^* = \rho\sigma_0^3$ is the reduced density, $X^* = \frac{3}{4}Q^{*2}$ and $Q^* = Q/(kT\sigma_0^5)^{1/2}$ is the reduced quadrupole moment. The factor J , which depends only on the shape parameter κ , is given by

$$J(\kappa) = (4\pi)^{-2} \int \left[\frac{\sigma(\omega_1, \omega_2)}{\sigma_0} \right]^{-2n+3} \Phi^2(\omega_1, \omega_2) d\omega_1 d\omega_2. \tag{7}$$

For HGOQ fluids $n = 5$ and Φ is for the angle-dependent part of the potential u_Q .

The third-order contribution to the Helmholtz function consists of two terms $A_3^{(1)}$ and $A_3^{(2)}$. The former has the form

$$\frac{A_3^{(1)}}{NkT} = \frac{1}{3} \pi \rho^* X^{*3} K(\kappa) \int_1^\infty g^{hs}(x) x^{-3n+2} dx, \tag{8}$$

where

$$K(\kappa) = (4\pi)^{-2} \int \left[\frac{\sigma(\omega_1, \omega_2)}{\sigma_0} \right]^{-3n+3} \Phi^3(\omega_1, \omega_2) d\omega_1 d\omega_2. \tag{9}$$

The latter term is (within the superposition approximation)

$$\frac{A_3^{(2)}}{NkT} = \frac{4}{3} \pi^2 \rho^{*2} X^{*3} \int_{(\Delta)} M(\kappa, \alpha_1, \alpha_2) g^{hs}(q) g^{hs}(s) g^{hs}(t) q^{-n+1} s^{-n+1} t^{-n+1} dq ds dt. \tag{10}$$

Here (Δ) denotes integration over q, s and t , which form a triangle with angles α_1, α_2 and α_3 , and

$$M(\kappa, \alpha_1, \alpha_2) = (4\pi)^{-3} \int \Psi(\omega_1, \omega_2) \Psi(\omega_1, \omega_3) \Psi(\omega_2, \omega_3) d\omega_1 d\omega_2 d\omega_3, \tag{11}$$

where

$$\Psi(\omega_i, \omega_j) = \Phi(\omega_i, \omega_j) \left[\frac{\sigma(\omega_i, \omega_j)}{\sigma_0} \right]^{n-1}. \tag{12}$$

The integrals $J(\kappa)$ and $K(\kappa)$ were evaluated by numerical integration for $\kappa = 1-2.5$; they are given in [10]. The calculation of the integral in (11) is more demanding because of the dependence of M on the angles of the triangle formed by q, s and t . In the case $\kappa = 1$ (i.e. for hard spheres), an analytical expression is available for M as a function of the angles α_1, α_2 and α_3 [5]:

$$M(1, \alpha_1, \alpha_2) = \frac{1}{450} \{ -27 + 220 \cos \alpha_1 \cos \alpha_2 \cos \alpha_3 + 490 \cos 2\alpha_1 \cos 2\alpha_2 \cos 2\alpha_3 + 175[\cos 2(\alpha_1 - \alpha_2) + \cos 2(\alpha_1 - \alpha_3) + \cos 2(\alpha_2 - \alpha_3)] \}. \tag{13}$$

Numerical integration for general κ is prohibitively time-consuming. In [10] we neglected the $A_3^{(2)}$ term completely after finding the value of $M(\kappa, \alpha_1, \alpha_2)$ for $\kappa = 1.792$ at several chosen values of α_1, α_2 and α_3 considerably smaller than those for $\kappa = 1$. Here we have employed the idea of an effective quadrupole moment embedded on the hard spheres to estimate the value of the $A_3^{(2)}$ term (see section 3). To this end, we evaluated the integral in (10) for $\kappa = 1$ and several densities and fitted the resulting values to the formula $I_M = 0.01555e^{4.3158\eta}$.

Knowledge of A_2 and A_3 allows us to determine the contribution due to the quadrupole moment $A - A^{HGO}$, either from the perturbation expansion

$$\frac{A - A^{HGO}}{NkT} = \frac{A_2}{NkT} + \frac{A_3^{(1)} + A_3^{(2)}}{NkT}, \tag{14}$$

or from the Padé approximant

$$\frac{A - A^{\text{HGO}}}{NkT} = \frac{A_2}{NkT} \left(1 - \frac{A_3^{(1)} + A_3^{(2)}}{A_2} \right)^{-1}. \quad (15)$$

To obtain the contribution of the internal energy, $U - U^{\text{HGO}}$, which is equal to the residual internal energy, one can differentiate (14) or (15) (with respect to X^* , followed by multiplication by X^*), eventually just writing the Padé approximant for the internal energy; however, we avoid this method as being less consistent.

The compressibility factor $Z = \beta P/\rho$ is given by the sum of two terms: the compressibility factor of the HGO fluid and the contribution of the quadrupole moment. The latter term follows from the derivative of (14) or (15) with respect to density; the former can be determined from the hard-convex-body equation of state applied to hard ellipsoids of revolution (HER) corresponding to the HGO fluid under consideration. There are two methods of assigning HER to the given HGO, one due to Rigby [15] and the other to one of the present authors [13]; the methods differ in the criterion used to define the corresponding HER fluid; in the former case the volume $V^{\text{HER}} = V^{\text{HGO}}$, while in the latter $\alpha^{\text{HER}} = \alpha^{\text{HGO}}$; the remaining quantity is determined from the expression for the second virial coefficient. As the latter method yields slightly better agreement with recent MC data on HGO systems, we employed it here too. Thus the parameter of non-sphericity, α , of the corresponding HER is determined for the given value of κ (of HGO) and the corresponding volume from the expression

$$V^{\text{HER}}(1 + 3\alpha) = \frac{2}{3} \pi \sigma_0^3 \left\langle \left(\frac{\sigma}{\sigma_0} \right)^3 \right\rangle_{\text{geom}}, \quad (16)$$

where $\langle \rangle_{\text{geom}}$ denotes the average over all orientations of two HGO particles; $\langle (\sigma/\sigma_0)^3 \rangle_{\text{geom}}$ can be calculated either from the expansion in terms of χ [16] or from the Padé approximant [13]. The equation of state of hard convex bodies [17] then yields a fair prediction of the HGO compressibility factor.

3. Simulations

The standard Monte Carlo simulation technique with the Metropolis sampling and periodic conditions [18, 19] was used in this study. We considered $N = 256$ particles interacting via the potential (1) in a cubic box. At the start the molecules filled the volume of the box completely; by changing the molecular size, the densities corresponding to packing fractions $\eta = 0.3, 0.4$ and 0.425 were obtained. In accordance with the form of the pair potential (which consists of a hard part and a continuous quadrupolar contribution), one has to determine the contribution of the quadrupolar moment to internal energy and pressure, U^{Q} and P^{Q} , i.e.

$$\frac{U^{\text{Q}}}{NkT} = \left\langle \sum_{i < j} u_{ij}^{\text{Q}}(r_{ij}, \omega_i, \omega_j) \right\rangle, \quad (17)$$

$$Z^{\text{Q}} = \frac{P^{\text{Q}}}{\rho kT} = \frac{5}{3} \frac{U^{\text{Q}}}{NkT}, \quad (18)$$

(where $\langle \rangle$ now denotes the canonical average), and then the contribution to the compressibility factor due to the discontinuous HGO part of the potential; this

follows from the pressure equation of state

$$Z^{\text{HGO}} = 1 + \frac{2}{3} \pi \rho \sigma_0^3 g^{\text{av}}(1) \left\langle \left(\frac{\sigma}{\sigma_0} \right)^3 \right\rangle_{\text{geom}}. \tag{19}$$

The average distribution function at contact, $g^{\text{av}}(1)$, can be obtained during the simulation from

$$g^{\text{av}}(x) = \frac{2 \langle \mathcal{N}(x) \rangle}{N \rho [V(x + \frac{1}{2} \Delta x) - V(x - \frac{1}{2} \Delta x)]}, \tag{20}$$

where

$$V(x) = \frac{4}{3} \pi \left\langle \left(\frac{\sigma}{\sigma_0} \right)^3 \right\rangle_{\text{geom}} x^3 \tag{21}$$

and \mathcal{N} is the number of pairs with the given distance.

The form of (19) resembles the pressure equation of state of hard spheres and reduces to it in the case $\kappa = 1$. Equation (19), together with (20), is only another variant of the expression employed by Rigby [15]; the present form is slightly simpler in simulation applications. To check the consistency of both variants, we considered the case $Q = 0$ and $\eta = 0.4$ and used the above prescriptions; we obtained fair agreement with Rigby's value.

In the process of simulation the quadrupolar interaction was truncated at $2.5\sigma_0$; in the case of the highest density we also performed a run with a cut-off length $3.0\sigma_0$; we found only insubstantial differences in internal energy and pressure. A typical run consisted of 2000–3000 trial moves per particle in the initial period, followed by 3000–4000 in the equilibrium part. For the highest density and highest Q value 6000 trial moves were necessary in order to reach equilibrium. During this equilibrium part of each run the residual internal energy, pressure and structural characteristics (spherical-harmonic coefficients and average distribution function) were determined for every 10th trial move per particle. The acceptance ratio was kept in the range of 30–50%.

In order to check the basic assumptions (4), we performed simulations in the pure HGO system and determined the distribution function g^{av} from the average number of particles with the given distance x , as well as the corresponding higher moments. We found the first-order term to be zero within statistical uncertainty. The second-order MC term agreed well with the theoretical value of the perturbation term; because of large statistical errors, it was impossible to determine the third-order term. The properties of the A_1 and A_2 terms provide some evidence in favour of the first part of (4). The behaviour of the average distribution function of HGO fluids with $\kappa = 1.792$ and 2.2 at packing fraction $\eta = 0.4$ is compared in figures 1 and 2 with the radial distribution function of hard spheres at the same η . It is obvious that the g^{av} curves for $\kappa = 1.792$ and 2.2 differ only slightly; they agree well with the pair distribution function of hard spheres. This testifies to the correctness of the second part of (4). The agreement is very good for $x = 1-1.5$, i.e. in the most important distance interval for the determination of the integrals in (6) and (8) in the case of the quadrupolar moment. For the interval $x = 1.5-2.5$ the differences increased with increasing coefficient κ . For $\kappa = 2.2$ we evaluated the integrals in (6) and (8) on the basis of the MC values of g^{av} , and obtained 0.3223 and 0.2252 compared with 0.3159 and 0.2188 respectively based on g^{hs} . (In passing, we note that in [10] slightly higher values of integrals were employed, resulting from the use of a coarser integration

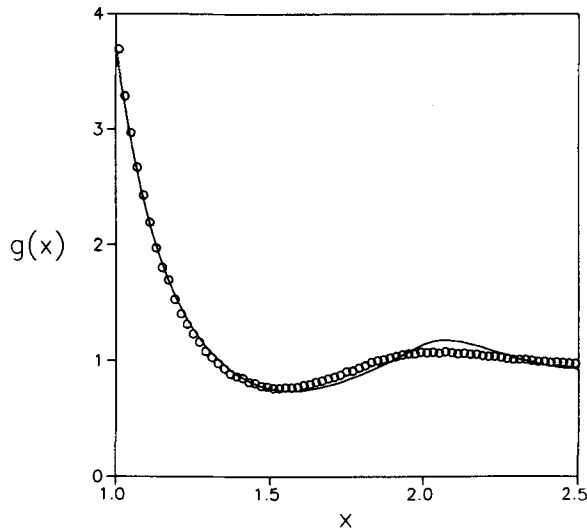


Figure 1. Comparison between the average distribution function of the HGO fluid with $\kappa = 1.792$ (O) and the pair correlation function of hard spheres (—) for $\eta = 0.4$.

grid.) Values of the compressibility factor (for $Q = 0$) 7.96 and 8.79 were found, compared with theoretical values 8.07 and 9.13 respectively. The good agreement between theoretical and experimental compressibility factors at lower κ is obvious, as is the poor agreement at higher value κ .

Next, simulations were performed in the HGOQ system with $\kappa = 1.792$. This was used in [10] as a model corresponding to hard dumbbells of $l = 0.6\sigma_0$, considered in the work of Wojcik and Gubbins (WG) [6] as well as in that of Lombardero *et al.* (LLA) [7]. (The MC data of WG were obtained by considering point charges, and thus correspond to quadrupole + higher moments, whereas those of LLA correspond to

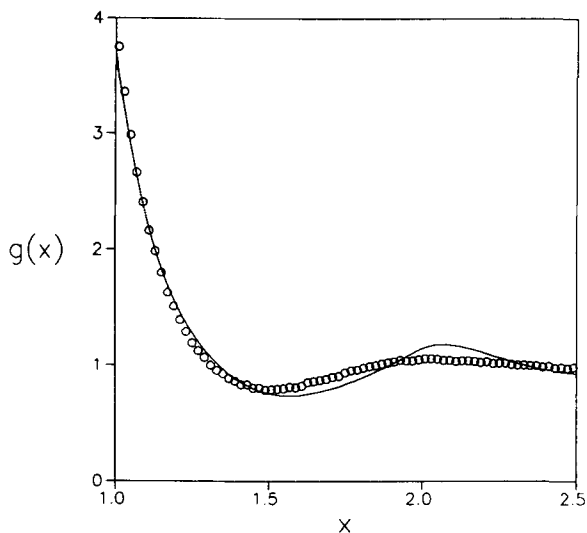


Figure 2. Comparison between the average distribution function of the HGO fluid with $\kappa = 2.2$ (O) and the pair distribution function of hard spheres (—) for $\eta = 0.4$.

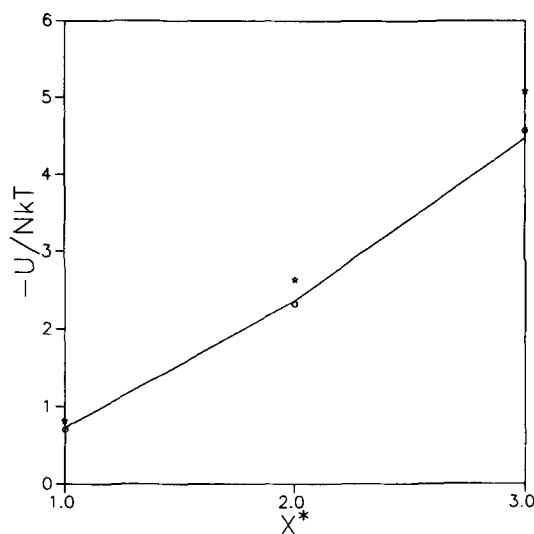


Figure 3. Dependence of the residual internal energy on the quadrupolar moment: ○, WG; ☆, LLA; —, this work.

an ideal quadrupole moment.) Three values of Q^* were chosen, namely 1.1497, 1.6260 and 1.9914, which correspond to values of the effective quadrupole moment of WG $Q_{WG}^2 = 0.5, 1.0$ and 1.5 and approximately to $Q_{LLA}^2 = 1, 2$ and 3. Figure 3 shows the contribution to the internal energy at a given Q^2 following from [6, 7] and from this study of an HGOQ fluid. Surprisingly good agreement is found between the HGOQ values of energy and those of WG for quadrupolar hard dumbbells, whereas the LLA results are systematically more negative. From the dependence of the residual internal energy on X^* , the values of the Helmholtz function were determined using the method proposed by Patey and Valleau [5]. They considered the form of the Padé approximant as a useful fitting function and evaluated its two parameters from the MC values of the residual energy. The accuracy of the residual internal energy obtained and the contribution to the Helmholtz function is 0.01 or 1%, whichever is higher; the error bars of the compressibility factor obtained as a difference of two large terms are larger. The absolute value of the quadrupolar-moment contribution to the compressibility factor increases with increasing X^* in the same way as the residual energy; the increase in the HGO term is due to the increase in the contact value of the average distribution function g^{av} . The behaviour of the function g^{av} for three values of X^* at $\eta = 0.4$ is shown in figure 4. The dependence of g^{av} on the value of the quadrupole moment is similar to that found for quadrupolar hard spheres [5]. The resulting data for $(A - A^{HGO})/NkT$, $(U - U^{HGO})/NkT$ and $\beta P/\rho$ of the HGOQ system with $\kappa = 1.792$ are listed in tables 1–3 as functions of the packing fraction η and reduced quadrupole moment X^* .

In table 4 Monte Carlo data are given for the HGOQ fluid with $\kappa = 2.2$ at the reduced density 0.3472 corresponding to the packing fraction $\eta = 0.4$. It is evident that with increasing κ at the same packing fraction and reduced quadrupole moment the absolute values of all contributions to the thermodynamic functions decrease.

4. Calculations

Theoretical values of the residual internal energy and Helmholtz functions were determined from third-order perturbation theory, employing (6)–(10). The values of

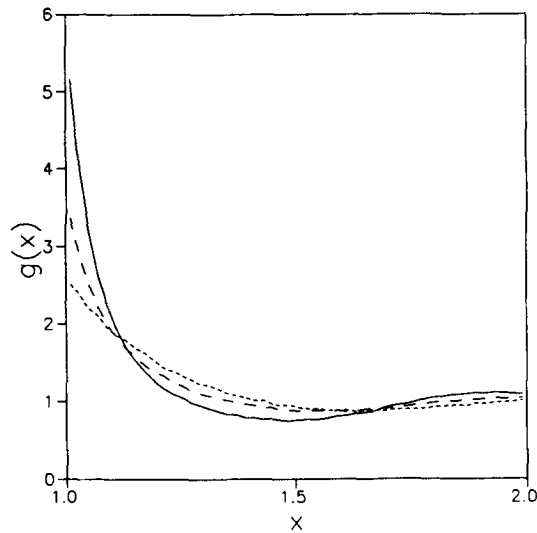


Figure 4. The average distribution function of HGO fluids with $X^* = 0.9914$ (.), 1.9828 (---) and 2.9743 (—).

the integrals $J_Q(\kappa)$ and $K_Q(\kappa)$ for values of $\kappa = 1.792$ and 2.2 were taken from [10]; their values were 1.0405 and 0.472 , and/or 0.7284 and 0.4363 . To determine the integrals with respect to x in the terms A_2 and $A_3^{(1)}$, the Padé approximants given by Rasaiah *et al.* [20] can be used. However, to yield better accuracy, we evaluated them by numerical integration. First, we neglected the term $A_3^{(2)}$ completely and obtained $A - A^{\text{HGO}}$ either as the sum of A_2 and $A_3^{(2)}$ or from the Padé approximant. The theoretical values obtained in this way are given in the left-hand columns of tables 1–4 for three values of X^* . Next, we tried to estimate $A_3^{(2)}$ with the help of the expression for a special case of the polar HGO fluid: quadrupolar hard spheres (HS). The σ_{eff} parameter of the effective HS was taken as that giving the same volume as the HGO body, i.e. $\sigma_{\text{eff}}^3 = \kappa\sigma_0^3$. Thus, to obtain an estimate of $A_3^{(2)}$ at given κ , we took in (10) the value of the integral for quadrupolar hard spheres at the same value of η and divided it by $\kappa^{15/3}$. A similar approach for A_2 at $\kappa = 1.792$ yielded approximately

Table 1. Contribution to the Helmholtz energy, $-A_Q/NkT$, of quadrupolar HGO fluids ($X^* = 3Q^2/4kT\sigma_0^3$).

	$X^* = 0.9914$		$X^* = 1.9828$		$X^* = 2.9743$	
$\eta = 0.30$						
Theory sum	0.24	0.23	0.85	0.82	1.68	1.57
Padé approximant	0.24	0.24	0.88	0.86	1.84	1.78
Monte Carlo	0.24 ± 0.01		0.88 ± 0.01		1.85 ± 0.01	
$\eta = 0.40$						
Theory sum	0.39	0.38	1.37	1.28	2.68	2.38
Padé approximant	0.39	0.38	1.43	1.38	2.97	2.81
Monte Carlo	0.39 ± 0.01		1.36 ± 0.01		2.70 ± 0.01	
$\eta = 0.425$						
Theory sum	0.43	0.42	1.53	1.42	2.98	2.60
Padé approximant	0.44	0.43	1.60	1.53	3.31	3.11
Monte Carlo	0.44 ± 0.03		1.49 ± 0.05		2.96 ± 0.08	

Table 2. Contribution to the internal energy, $-U_Q/NkT$, of the quadrupolar HGO fluid ($X^* = 3Q^2/4kT\sigma_0^3$).

	$X^* = 0.9914$		$X^* = 1.9828$		$X^* = 2.9743$	
$\eta = 0.30$						
Theory sum	0.45	0.44	1.49	1.40	2.66	2.34
Padé approximant	0.46	0.45	1.62	1.57	3.26	3.10
Monte Carlo	0.46 \pm 0.01		2.62 \pm 0.01		3.31 \pm 0.01	
$\eta = 0.40$						
Theory sum	0.73	0.70	2.38	2.12	4.15	3.26
Padé approximant	0.75	0.70	2.62	2.47	5.23	4.83
Monte Carlo	0.73 \pm 0.01		2.36 \pm 0.01		4.47 \pm 0.01	
$\eta = 0.425$						
Theory sum	0.82	0.77	2.65	2.32	4.58	3.46
Padé approximant	0.83	0.80	2.92	2.73	5.82	5.32
Monte Carlo	0.79 \pm 0.01		2.57 \pm 0.01		4.88 \pm 0.05	

three-quarters of the correct value of $J(\kappa)$; this ratio gives rough information about the quality of the approximation used. Results of the calculation of $(A - A^{HGO})/NkT$, $(U - U^{HGO})/NkT$ and $\beta P/\rho$ with the $A_3^{(2)}$ term included are given in the right-hand columns of tables 1-4.

From comparison with the MC data it can be seen that in the case of the neglected $A_3^{(2)}$ term the equilibrium behaviour of the HGOQ fluid is similar to that found previously [13] for quadrupolar hard dumbbells. When the estimates of the $A_3^{(2)}$ or $U_3^{(2)}$ terms are included in the expressions for the Helmholtz function or internal energy, their theoretical values became less negative, both in the series expansion and the Padé approximant. Whereas (14) and the corresponding expression for internal energy give better results when the $A_3^{(2)}$ term is neglected, in the case of the Padé approximant the inclusion of this term improves agreement with the Monte Carlo data. At higher densities the Padé values are slightly more negative than the MC values, indicating that the approximation employed yields a lower bond on the $A_3^{(2)}$ term and that its exact evaluation would yield generally better agreement of theory with the present MC data. Similar conclusions can also be drawn for the compressibility factor, where the inclusion of the $A_3^{(2)}$ term leads to an increase in the theoretical value, and where

Table 3. Compressibility factor $\beta P/\rho$ of the quadrupolar HGO fluid ($X^* = 3Q^2/4kT\sigma_0^3$).

	$X^* = 0.9914$		$X^* = 1.9828$		$X^* = 2.9743$	
$\eta = 0.30$						
Theory sum	4.12	4.13	3.16	3.27	1.91	2.26
Padé approximant	4.12	4.13	3.10	3.17	1.61	1.80
Monte Carlo	4.11 \pm 0.04		3.12 \pm 0.06		1.92 \pm 0.08	
$\eta = 0.40$						
Theory sum	7.37	7.42	5.66	5.99	3.49	4.59
Padé approximant	7.37	7.40	5.52	5.73	2.83	3.40
Monte Carlo	7.30 \pm 0.10		5.99 \pm 0.15		4.02 \pm 0.20	
$\eta = 0.425$						
Theory sum	8.63	8.68	6.67	7.10	4.22	5.65
Padé approximant	8.62	8.66	6.50	6.77	3.43	4.16
Monte Carlo	8.62 \pm 0.12		7.05 \pm 0.17		4.68 \pm 0.30	

Table 4. Contribution due to the permanent quadrupole moment to thermodynamic functions and the compressibility factor of the HGOQ fluid with $\kappa = 2.2$ and $\eta = 0.4$ ($X^* = 3Q^2/4kT\sigma_0^5$).

	$X^* = 0.9914$		$X^* = 1.9828$		$X^* = 2.9743$	
<i>- A/NkT</i>						
Theory sum	0.21	0.21	0.72	0.70	1.31	1.24
Padé approximant	0.22	0.21	0.77	0.76	1.57	1.54
Monte Carlo	0.24 ± 0.02		0.87 ± 0.04		1.76 ± 0.06	
<i>- U/NkT</i>						
Theory sum	0.39	0.38	1.16	1.10	1.70	1.49
Padé approximant	0.41	0.40	1.38	1.35	2.69	2.60
Monte Carlo	0.46 ± 0.01		1.59 ± 0.02		2.95 ± 0.04	
<i>βP/ρ</i>						
Theory sum	8.76	8.77	7.90	7.98	6.98	7.25
Padé approximant	8.75	8.76	7.77	7.81	6.38	6.51
Monte Carlo	8.56 ± 0.10		7.35 ± 0.15		5.97 ± 0.30	

neglect of this term leads to Padé-approximant predictions of Z that are too low. All of the above conclusions hold true for the HGOQ system with $\kappa = 1.792$. For the system with $\kappa = 2.2$ the agreement between theoretical and pseudo-experimental data at higher values of Q is worse. As is obvious from figure 2, the approximation of the average distribution function (5) in the case $\kappa = 2.2$ is less good than in the case $\kappa = 1.792$. As a result, both the A_2 and $A_3^{(2)}$ terms are underestimated, and this leads to an underestimate of the theoretical values of the Helmholtz function and internal energy. In the case of the compressibility factor of the HGOQ system the main source of error is inaccuracy of the evaluation of the compressibility factor of the HGO system, which is about one-third higher than the experimental value. Improvement in the knowledge of the HGO equation of state would probably improve the overall agreement of the theory with the MC data obtained.

5. Conclusion

In this paper the results of Monte Carlo simulations in a system of quadrupolar hard Gaussian-overlap fluids are reported at several densities and values of the reduced quadrupole moment. Two values of the shape parameter have been considered, 1.792 and 2.2. The former corresponds to the previously studied systems of quadrupolar hard dumbbells with length $l^* = 0.6$. On comparing the pseudo-experimental data of these two systems, differing in the shape of the hard body (one is the simplest fused hard-sphere model, the other a convex-like body), the similarity of the results for the thermodynamic functions is striking. This is further evidence in favour of the idea of only moderate differences between the equilibrium behaviour of fluids with the interaction-site form of potential and those with the convex-molecule form, in spite of considerable formal differences. Comparison of the calculated residual thermodynamic functions with the simulation results reveals good agreement over the whole range of densities for values of the reduced quadrupole moment X^* not exceeding $= 2$. For higher X^* the estimate of the $A_3^{(2)}$ term is not sufficiently accurate; also, the limitations of the use of the Padé approximant for thermodynamic functions of polar fluids manifest themselves more seriously [5].

The study of the HGO system with $\kappa = 2.2$ was made with the aim of checking the capability of the theory to deal with more elongated molecules. In spite of poorer accord of theoretical and simulation data (from reasons discussed in the previous paragraph), the theory still yields a very useful description of the equilibrium behaviour of considerably non-spherical molecule systems.

In conclusion, one can say that the proposed method of describing systems of polar non-spherical (convex) molecules proves to be both simple and fairly accurate.

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