

## Monte Carlo study of quadrupolar Kihara fluids

By CARLOS VEGA

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad  
Complutense de Madrid, E-28040 Madrid, Spain

KEITH E. GUBBINS

School of Chemical Engineering, Cornell University, Olin Hall, Ithaca,  
New York 14853, USA

*(Received 10 June 1991; accepted 13 August 1991)*

Monte Carlo simulations of linear Kihara fluids with embedded point quadrupoles are reported for several elongations and values of the quadrupole. The quadrupolar contribution to the Helmholtz free energy is obtained and the effect of quadrupole on the structure is studied. The data obtained should be useful to check perturbation theories of convex quadrupolar Kihara fluids. An attempt to model carbon dioxide with the quadrupolar Kihara model has also been carried out. It is shown that accounting for the quadrupole moment in the model improves the agreement with measured properties. Overall this agreement is found to be good. These results encourage further theoretical work with this potential model.

### 1. Introduction

During the last decade the statistical mechanics of linear nonpolar fluids has been successfully developed for several potential models. For the site-site model there are several perturbation schemes that involve extensions of the Weeks-Chandler-Andersen (WCA) [1] method to fluids of linear [2-7] and nonlinear molecules [8], and also integral equations [9]. Perturbation theories have also been developed [10-13] for the Gaussian potential model [14]. Finally, for the Kihara potential model [15] there are also successful perturbation theories [16-18], thus for site-site, Gaussian overlap and Kihara model fluids there are now quite good theories.

For polar fluids the situation is less satisfactory. Although the Pople-Stell-Gubbins-Gray theory [19] has given very good results for spherical or quasi-spherical polar molecules, the results are not so satisfactory for molecules possessing both nonspherical shape forces and long range multipole interactions. Attempts based on WCA first-order theories give rather poor results [20]. Most previous studies of fluids of linear polar or multipolar fluids have thus been carried out by simulation methods. These include simulations of the two-centre Lennard-Jones plus point quadrupole model (2CLJQ) [20-23], quadrupolar hard dumbbells (HDQ) [24, 25] and their mixtures [26], and the hard Gaussian overlap with point quadrupole (HGOQ) [27]. There is no reported simulation study of multipolar Kihara molecules.

In this work we study a fluid consisting of molecules that interact with a Kihara potential having an embedded point quadrupole (KQ). Such a fluid provides a simple model for such important real fluids as  $N_2$ ,  $Cl_2$  and  $CO_2$ . The utility of such a model is twofold. First, it allows a semiquantitative description of the thermodynamics of real fluids in the liquid phase, and second, because of its simplicity, it constitutes

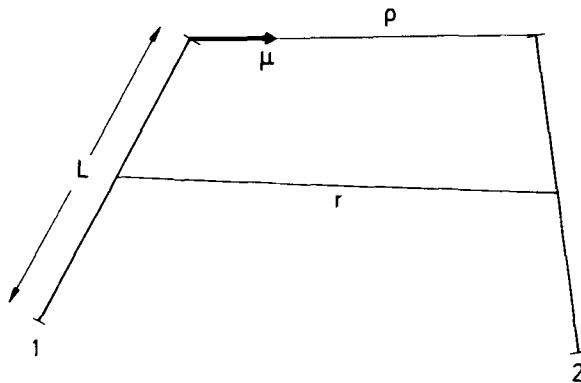


Figure 1. (a) Geometry of the linear core used in this work. The shortest distance between the cores is  $\rho$ . We also show the unit vector  $\mu$  in the direction of  $\rho$ .

a tractable model for theoretical calculations. In fact, Boublik [28] has recently developed a promising perturbation scheme for Kihara quadrupolar fluids based on the Pople–Stell–Gubbins–Gray theory [19] with a nonspherical reference system. The theory was applied to a linear KQ model but due to the lack of simulation data it could not be tested against simulation results of the same model. In this work we first present simulation results for the KQ model for several state conditions and quadrupole strengths which can be useful to test theories for this kind of molecules. We then apply the model to  $\text{CO}_2$ , and compare simulation results with experimental data.

The scheme of the paper is as follows. In section 2 we describe the potential models that are used as well as the simulation methodology. In section 3 we report the thermodynamic and structural results of the simulations. Section 4 contains an attempt to describe  $\text{CO}_2$  with the Kihara quadrupolar model, and finally section 5 gives the main conclusions of this work.

## 2. Simulation method

We have carried out Monte Carlo (MC) simulations of quadrupolar linear molecules interacting through two different types of potential. The first one, which we shall call Kihara with quadrupole (KQ), is given by:

$$u_{\text{KQ}}(r, \omega_1, \omega_2) = u_{\text{K}}(r, \omega_1, \omega_2) + u_{\text{Q}}(r, \omega_1, \omega_2), \quad (1)$$

where  $r$  is the distance between the centres of mass of the molecules,  $\omega_1 = (\theta_1, \phi_1)$  defines the polar angles of molecule 1 and analogously for  $\omega_2$ . The potentials  $u_{\text{K}}$  and  $u_{\text{Q}}$  are given by

$$u_{\text{K}} = 4\varepsilon[(\sigma/\rho)^{1/2} - (\sigma/\rho)^6], \quad (2)$$

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

where  $\varepsilon$  is the well depth of the dispersion forces,  $\sigma$  the value of  $\rho$  where  $u_{\text{K}}$  is zero,  $Q$  the quadrupole moment,  $c_i = \cos \theta_i$ ,  $s_i = \sin \theta_i$  and  $c = \cos(\phi_1 - \phi_2)$ . In (3), the polar axis connects the centres of mass of the molecules. The shortest distance between the cores of the two molecules is denoted as  $\rho$ . In this work we shall use a linear rod as the molecular core (see figure 1). Algorithms to evaluate the shortest distance between two rods are available elsewhere [29]. The presence of the quad-

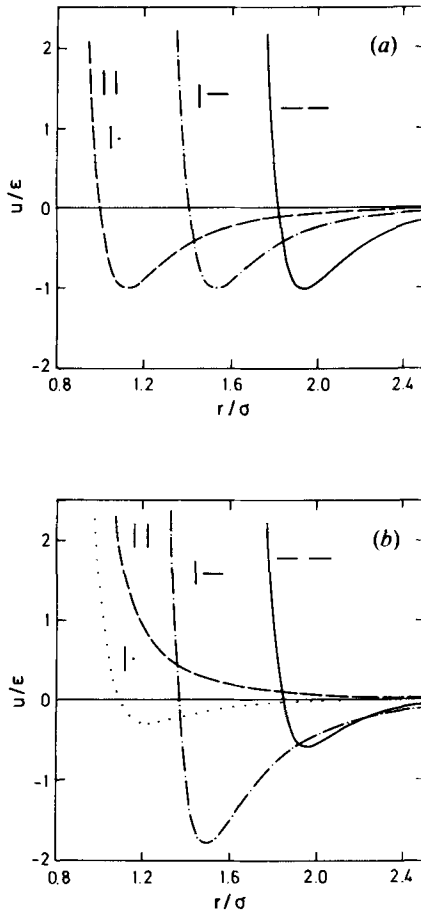


Figure 2. The intermolecular pair potential for several relative orientations. Solid line, aligned configuration ( $\theta_1 = 0, \theta_2 = 0, \phi_{12} = \text{undefined}$ ), dashed line parallel configuration ( $\theta_1 = \pi/2, \theta_2 = \pi/2, \phi_{12} = 0$ ), dot-dashed line T configuration ( $\theta_1 = \pi/2, \theta_2 = 0, \phi_{12} = \text{undefined}$ ), dotted cross configuration ( $\theta_1 = \pi/2, \theta_2 = \pi/2, \phi_{12} = \pi/2$ ). The elongation of the molecule is  $L^* = L/\sigma = 0.8118$ . (a)  $Q^{*2} = 0$  (In this case the parallel and cross configuration are indistinguishable) (b)  $Q^{*2} = 2$ .

rupole strongly modifies the well depth of the pair potential for every relative orientation. This is shown in figure 2. The T configuration is favoured by the presence of the quadrupole. If the WCA decomposition is applied to the potential of (2) [17] and we add a quadrupolar term we obtain the WCA with quadrupole fluid (WCAQ) which is given by

$$u_{\text{WCAQ}} = u_{\text{WCA}} + u_Q, \tag{4}$$

where  $u_{\text{WCA}}$  is given by

$$u_{\text{WCA}} = 4\epsilon[(\sigma/\rho)^{12} - (\sigma/\rho)^6] + \epsilon, \quad \rho < 2^{1/6}\sigma, \tag{5}$$

$$u_{\text{WCA}} = 0, \quad \rho > 2^{1/6}\sigma. \tag{6}$$

The potentials,  $u_{\text{KQ}}$  and  $u_{\text{WCAQ}}$  constitute the two models studied in this work. To study their thermodynamic properties we have carried out MC simulations according

to the standard procedure of Metropolis *et al.* [30]. In all the simulations we have used 256 particles in a cubic box with periodic boundary conditions. We started all the runs from an  $\alpha$  fcc lattice. A run consist of an initial period of 3000–5000 trial moves per particle to reach equilibrium followed by a period of 6000–10000 trial moves per particle to obtained 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 35–55%. An order parameter [31] was evaluated during the runs to be sure that the system was orientationally equilibrated.

The pressure  $p$  or residual internal energy  $U$  is obtained by adding a long range contribution to the value of the property evaluated during the run. We neglect the contribution of the quadrupole to the long range correction and only consider the long range correction due to the dispersion forces. A similar treatment was used in [20]. For the WCAQ fluid we did not add any long range contribution, since the dispersion forces are zero at long distances. For the KQ fluid this long range contribution was evaluated assuming a uniform fluid when  $\rho > \rho_c$  where  $\rho_c$  is the cutoff distance. Formulae for the evaluation of this long-range contribution to  $p$  and  $U$  are given in [32] and [33]. Typically  $\rho_c$  was chosen as  $B/2-L$  where  $B$  is the length of the side of the box and  $L$  the length of the rod. The transition probabilities along the Markov chain were, however, determined by truncating the pair interaction at  $\rho = 2.5\sigma$ . This procedure has already been used by Kantor and Boublik [34].

The structure of the system is described in terms of the intermolecular frame expansion coefficients of the pair correlation function  $g(r, \omega_1, \omega_2)$  in spherical harmonics [19]:

$$g(r, \omega_1, \omega_2) = 4\pi \sum_{l_1 l_2 m} g_{l_1 l_2 m}(r) Y_{l_1 m}(\omega_1) Y_{l_2 -m}(\omega_2), \quad (7)$$

where the polar axis is the one which connects the centres of mass of the molecules. The quadrupolar contribution to the internal energy  $U^Q$  can be easily formulated in terms of three of the coefficients of the pair correlation function as [21]:

$$U^Q = \frac{12\pi n Q^2}{5} \int (g_{220}(r) + \frac{4}{3}g_{221}(r) + \frac{1}{3}g_{222}(r))/r^3 dr, \quad (8)$$

where  $n$  is the number density. The quadrupolar contribution to the pressure,  $Z^Q$ , is given by

$$Z^Q = \frac{p^Q V}{NkT} = \frac{5U^Q}{3NkT}. \quad (9)$$

Another useful function for convex bodies is the average surface–surface correlation function  $g_{av}(\rho)$  [35]. This function represents an average of  $g(r, \omega_1, \omega_2)$  over all the distances and orientations which have a given surface to surface distance  $\rho$ . It can be easily evaluated from the recorded number of pair  $\langle N_{av}(\rho) \rangle$  in a given interval  $(\rho - \Delta\rho/2, \rho + \Delta\rho/2)$  of surface to surface distance as

$$g_{av}(\rho) = \frac{2\langle N_{av}(\rho) \rangle}{n(N-1)[V_{c+\rho+\Delta\rho/2+c} - V_{c+\rho-\Delta\rho/2+c}]}, \quad (10)$$

where  $V_{c+\rho+c}$  is the average volume over all the relative orientations of a combined body formed by the centre of molecule 2 when it moves around molecule 1 with a constant surface to surface distance. Formulae for the evaluation of  $V_{c+\rho+c}$  can be found in [35].

The contribution to  $p$  and  $U$  of any continuous potential depending on the shortest distance  $\rho$  between two convex bodies can be written in terms of  $g_{av}(\rho)$  as [32],

$$U^C/N = n/2 \int u_C(\rho)g_{av}(\rho)S_{c+\rho+c} d\rho, \quad C = K, WCA, \quad (11)$$

$$Z^C = 1 - \frac{n}{6kT} \int \langle r\mu \rangle_\rho g_{av}(\rho)S_{c+\rho+c} \left( \frac{du_C}{d\rho} \right) d\rho, \quad C = K, WCA, \quad (12)$$

where  $\mu$  is a unit vector in the direction of the shortest distance between the cores (see figure 1) and  $S_{c+\rho+c}$  is the average surface area of the body formed by molecule 2 moving around molecule 1 with a given surface-surface distance  $\rho$ .

We checked the program in three different ways. The first was to simulate a pure Kihara fluid without quadrupole and to compare with Boublik's results [16]. We did a run for  $T^* = [T/(\epsilon/k)] = 0.85$ ,  $n^* = n \sigma^3 = 0.3407$  and  $L^* = L/\sigma = 1$ . We obtained  $Z = 3.72$  and  $U/NkT = -5.83$ , which compares well with Boublik's reported results,  $Z = 3.70$  and  $U/NkT = -5.81$ . As a second check we obtained the quadrupolar contribution to the internal energy from (8) and compared with the one obtained in the run. We got  $U^Q/NkT = -1.071$  and  $U^Q/NkT = -1.068$ , respectively, with  $T^* = 1.50$ ,  $n^* = 0.36$ ,  $Q^{*2} = 3$  and  $L^* = 0.8118$ , where  $Q^* = Q/(\epsilon\sigma^5)^{1/2}$ . As a third check we did a run for  $T^* = 1.0935$ ,  $n^* = 0.8508$  and  $L^* = 0$ . For  $L^* = 0$  the  $u_{KQ}$  reduces to a Lennard-Jones fluid with point quadrupole. Our results were  $U^Q/NkT = -2.94$ ,  $U/NkT = -7.83$  which compares well with the results  $U^Q/NkT = -2.95$  and  $U/NkT = -7.83$  of [20].

A significant thermodynamic property is the change in Helmholtz free energy of the fluid due to the presence of the quadrupole,  $A^Q$ , at constant temperature and density. Using the quadrupole as the coupling parameter within Kirwood's formalism [36] this change is given by

$$A^Q = A(Q = Q) - A(Q = 0) = \int_0^Q \langle U^Q/Q^2 \rangle dQ^2. \quad (13)$$

To get  $A^Q$  we did several runs for a given  $L^*$ ,  $n^*$ ,  $T^*$  and different values of  $Q$ . From the runs  $U^Q$  was obtained and following the procedure of Patey *et al.* [37] we fitted  $U^Q/NkT$  to the expression:

$$\frac{U^Q}{NkT} = \frac{aQ^{*4}(bQ^{*2} + 2)}{(1 + bQ^{*2})^2}. \quad (14)$$

Substituting (14) in (13) one gets

$$\frac{A^Q}{NkT} = \frac{aQ^{*4}}{(1 + bQ^{*2})}. \quad (15)$$

### 3. Simulation results

#### 3.1. Thermodynamic properties

As our intention is to provide data to test theories we choose two different elongations to study. The first is  $L^* = 0.30$  and corresponds with the anisotropy of a  $N_2$  model. The second is  $L^* = 0.8118$  and corresponds to a  $CO_2$ -like elongation.

To apply (13) it is necessary that no phase transitions occurs along the integration path. Unfortunately the phase diagram of linear quadrupolar fluids is still unknown. As vapour pressures are typically low along the vapour-liquid coexistence curve we

Table 1. MC results for KQ and WCAQ fluids.  $Q^{*2} = Q^2/(\epsilon\sigma^5)$ .

Model	$L^*$	$T^*$	$n^*$	$Q^{*2}$	$U/NkT$	$U^Q/NkT$	$Z$
KQ	0.3	1.80	0.55	0	-2.381	0	3.706
KQ	0.3	1.80	0.55	0.5	-2.474	-0.094	3.554
KQ	0.3	1.80	0.55	1	-2.706	-0.358	3.335
KQ	0.3	1.80	0.55	2	-3.538	-1.303	2.546
KQ	0.3	1.80	0.55	3	-4.768	-2.696	1.356
WCAQ	0.3	1.80	0.55	0	0.712	0	7.190
WCAQ	0.3	1.80	0.55	0.5	0.625	-0.098	7.106
WCAQ	0.3	1.80	0.55	1	0.382	-0.365	6.830
WCAQ	0.3	1.80	0.55	2	-0.495	-1.335	5.872
WCAQ	0.3	1.80	0.55	3	-1.712	-2.712	4.685
KQ	0.8118	1.50	0.36	0	-2.773	0	4.173
KQ	0.8118	1.50	0.36	0.5	-2.809	-0.043	4.179
KQ	0.8118	1.50	0.36	1	-2.903	-0.151	4.075
KQ	0.8118	1.50	0.36	2	-3.230	-0.517	3.726
KQ	0.8118	1.50	0.36	3	-3.718	-1.071	3.269
KQ	0.8118	1.10	0.36	0	-4.068	0	3.253
KQ	0.8118	1.10	0.36	0.5	-4.127	-0.070	3.222
KQ	0.8118	1.10	0.36	1	-4.275	-0.247	3.157
KQ	0.8118	1.10	0.36	2	-4.840	-0.862	2.447
KQ	0.8118	1.10	0.36	3	-5.578	-1.697	1.699
WCAQ	0.8118	1.10	0.36	0	0.731	0	8.993
WCAQ	0.8118	1.10	0.36	0.5	0.663	-0.070	8.899
WCAQ	0.8118	1.10	0.36	1	0.494	-0.261	8.734
WCAQ	0.8118	1.10	0.36	2	-0.096	-0.897	8.021
WCAQ	0.8118	1.10	0.36	3	-0.888	-1.776	7.234

have chosen state points with relatively high density and with high pressure in order to avoid the liquid-vapour transition.

We have chosen  $T^* = 1.80$  and  $n^* = 0.55$  for  $L^* = 0.30$  as the first state point to study (SP1),  $T^* = 1.50$ ,  $n^* = 0.36$ ,  $L^* = 0.8118$  (SP2), and  $T^* = 1.10$ ,  $n^* = 0.36$  and  $L^* = 0.8118$  (SP3). For every state point we did simulations for  $Q^{*2} = 0, 0.5, 1, 2, 3$  with the  $u_{KQ}$  potential model. Furthermore we have studied the SP1 and SP3 with the  $u_{WCAQ}$  model.

Table 1 contains the results. From the results several conclusions can be drawn. The first is that the contribution to the internal energy from nonquadrupolar part of the potential (K or WCA) given by  $(U - U^Q)$  is not much affected by the presence of the quadrupole. In general it turns out that:

$$(U^C)_{Q=0} < (U^C)_{Q=Q} \quad C = K, WCA. \quad (16)$$

Similar results were obtained by Bohn *et al.* [20] for the 2CLJQ fluid. The contribution to the internal energy coming from  $u_K$  or  $u_{WCA}$  can be expressed in terms of  $g_{av}(\rho)$  (see (11)). The fact that this energy is not much affected by the presence of the quadrupole might suggest that  $g_{av}(\rho)$  may be only slightly modified by the presence of the quadrupole. We shall come to this point later. The contribution to the pressure from  $u_K$  or  $u_{WCA}$  is, however, strongly affected by the presence of the

Table 2. Coefficients  $a$  and  $b$  in (14) and (15) obtained from the MC data of table 1.

Model	$L^*$	$T^*$	$n^*$	$a$	$b$
KQ	0.30	1.80	0.55	-0.1958	0.0584
WCAQ	0.30	1.80	0.55	-0.2033	0.0751
KQ	0.8118	1.50	0.36	-0.0871	0.0988
KQ	0.8118	1.10	0.36	-0.1453	0.1147
WCAQ	0.8118	1.10	0.36	-0.1538	0.1183

quadrupole. In general it turns out that:

$$(Z^C)_{Q=0} < (Z^C)_{Q=Q}, \quad C = K, WCA. \tag{17}$$

The coefficients  $a$  and  $b$  of (14 and 15) are shown in table 2 for the different cases. In figure 3 we show  $A^Q$  and  $U^Q$  for the state points SP1, SP3 and the potential models KQ, WCAQ. It is interesting to point out that  $A^Q$ , the change in the Helmholtz free energy due to the presence of the quadrupole is very similar for the KQ and WCAQ models. Obviously the theoretical treatment of the WCAQ results is simpler than for KQ, due to the short range of the WCA potential. This suggests the following perturbation scheme:

$$A^{KQ} = A^K + A_K^Q, \tag{18}$$

where  $A^{KQ}$  is the Helmholtz free energy of the KQ fluid,  $A^K$  that of the nonpolar Kihara system K, and  $A_K^Q$  is the change in free energy due to Q. Figure 3 shows that

$$A_K^Q \simeq A_{WCA}^Q \tag{19}$$

is a good approximation where  $A_{WCA}^Q$  is the change in free energy that the WCA system undergoes due to the presence of the quadrupole.  $A^K$  can be obtained from perturbation theory [16-18, 38]. The only problem that remains is then the evaluation of  $A_{WCA}^Q$ .

### 3.2. Structural results

In the previous subsection we pointed out that  $U^C$  ( $C = K, WCA$ ) is not strongly modified by the presence of the quadrupole. That would suggest that  $g_{av}(\rho)$  remains almost unchanged. In figure 4 we show  $g_{av}(\rho)$  for the SP2 and for two values of  $Q^*$ , confirming this suggestion. There are, however, important changes in the preferred relative orientations with the presence of the quadrupole. In figure 5 we show the radial distribution function  $g(r)$  ( $g_{000}(r)$ ) and the  $g_{220}(r)$  coefficient for several values of the quadrupole in SP2. Both  $g(r)$  and  $g_{220}(r)$  are greatly changed by the presence of the quadrupole. The effect of the quadrupole on  $g(r)$  is to increase the height of the first peak and to delay the distance at which  $g(r)$  starts to be different from zero. The same changes were found for 2CLJQ [20] and for HDQ [24]. It is also interesting to note that the presence of the quadrupole in linear fluids strongly modifies the coefficients  $g_{000}(r)$  and  $g_{220}(r)$  as well as the rest of the coefficients of the expansion, while the presence of dipoles modifies only slightly  $g_{000}(r)$  and  $g_{220}(r)$ , and its major effect is on the coefficients  $g_{l_1 l_2 m}(r)$  with  $l_1, l_2$  odd as was found previously [39]. Therefore quadrupoles have a much greater effect than dipoles on the radial distribution function ( $g_{000}(r)$ ).

In figure 3 we show that  $A^Q$  is very similar for the KQ and the WCAQ fluid. That seems to indicate that for a given value of the quadrupole the structure of the KQ fluid is very similar to that one of the WCAQ system. In figure 6 we show  $g_{av}(\rho)$  for SP3

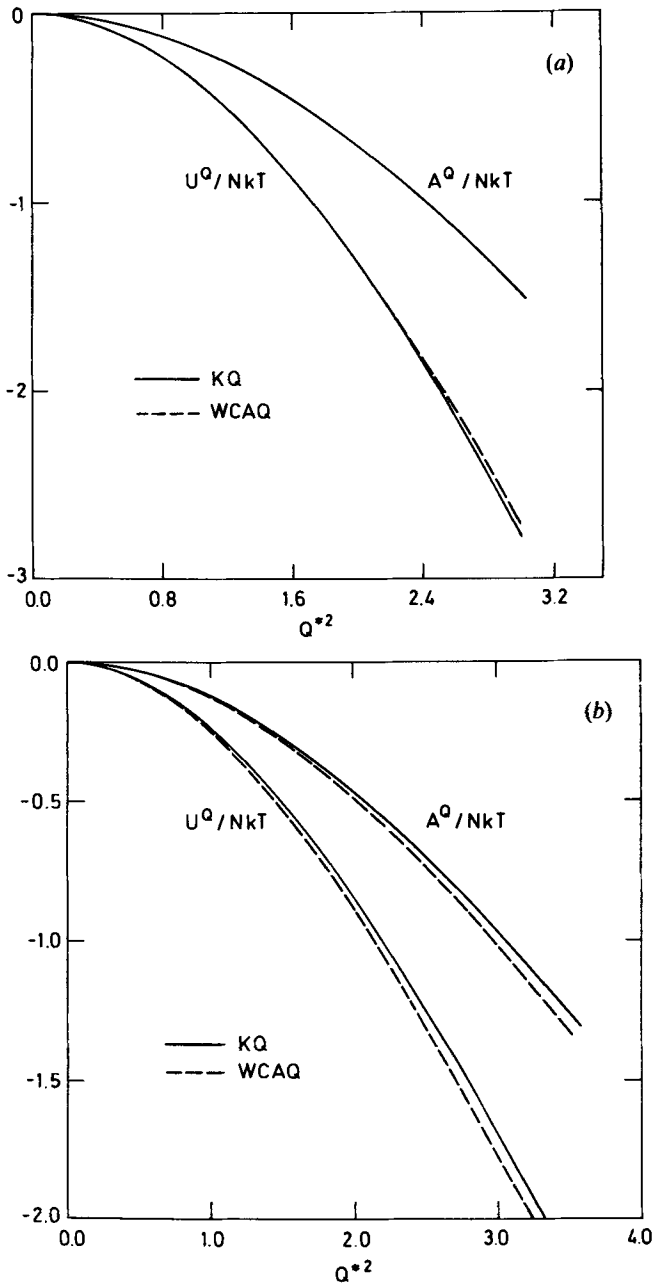


Figure 3. Contribution of the quadrupole to the internal energy  $U^Q$  and to the Helmholtz free energy  $A^Q$  (15). The solid line is for the KQ model, the dashed line for the WCAQ model. (a)  $L^* = 0.30$ ,  $n^* = 0.55$ ,  $T^* = 1.80$ , (b)  $L^* = 0.8118$ ,  $n^* = 0.36$ ,  $T^* = 1.10$ .



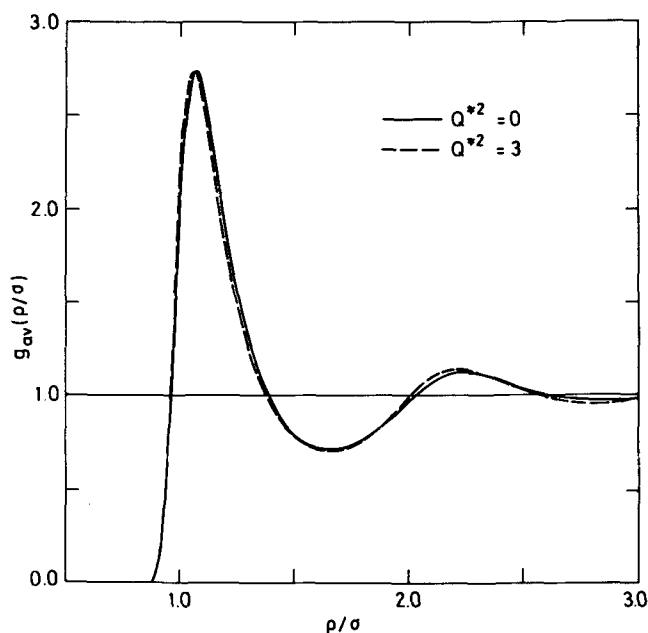


Figure 4. The surface-to-surface average correlation function  $g_{av}(\rho)$  (10) for  $L^* = 0.8118$ ,  $T^* = 1.50$ ,  $n^* = 0.36$  and the KQ model. Solid line  $Q^{*2} = 0$  and dashed line  $Q^{*2} = 3$ .

with  $Q^{*2} = 3$  for the KQ and WCAQ fluids. Although there are small differences, they are quite similar. This fact was already found for the Kihara nonpolar fluid [32] and seems to hold also for polar molecules.

We conclude that the presence of the quadrupole strongly modifies the coefficients  $g_{l_1 l_2 m}(r)$  but not  $g_{av}(\rho)$ . For a given  $Q$  value the structure of the KQ and WCAQ models are very similar at high densities.

#### 4. CO<sub>2</sub> with the Kihara plus quadrupole model

In this section we try to explore how well the thermodynamics of CO<sub>2</sub> can be described by the KQ model. We examine whether the inclusion of the quadrupole improves the thermodynamic description of CO<sub>2</sub>, and to what extent.

The independent variables are  $L^*$ ,  $Q^{*2}$ ,  $\epsilon$  and  $\sigma$ . To simplify the problem we took  $L^* = 0.8118$  as obtained from the Boublik [16] perturbation theory of CO<sub>2</sub>. This value agrees quite well with the value  $L^* = 0.782$  chosen by Kihara [40] in his study of CO<sub>2</sub> and with the value  $L^* = 0.793$  chosen by Fischer *et al.* [41] in their study of CO<sub>2</sub> with the 2CLJ fluid.

We study four values of  $Q^{*2}$ , namely  $Q^{*2} = 0, 1.5, 2.5, 3.5$ . For every value of  $Q^{*2}$ ,  $\epsilon$  and  $\sigma$  were determined as follows. As in [42]  $\epsilon$  was determined by fitting the residual internal energy at zero pressure obtained from MC to the experimental one. The experimental residual internal energy at zero pressure was obtained from extrapolation to zero pressure of an empirical equation of state [43] (EOS) for CO<sub>2</sub>. Once  $\epsilon$  had been obtained,  $\sigma$  was determined by minimizing the deviations between simulated and experimental pressures at four to six state points.

In table 3 we show the MC results used to determine the potential parameters. In table 4 we show the potential parameters obtained along with the quadrupole of the

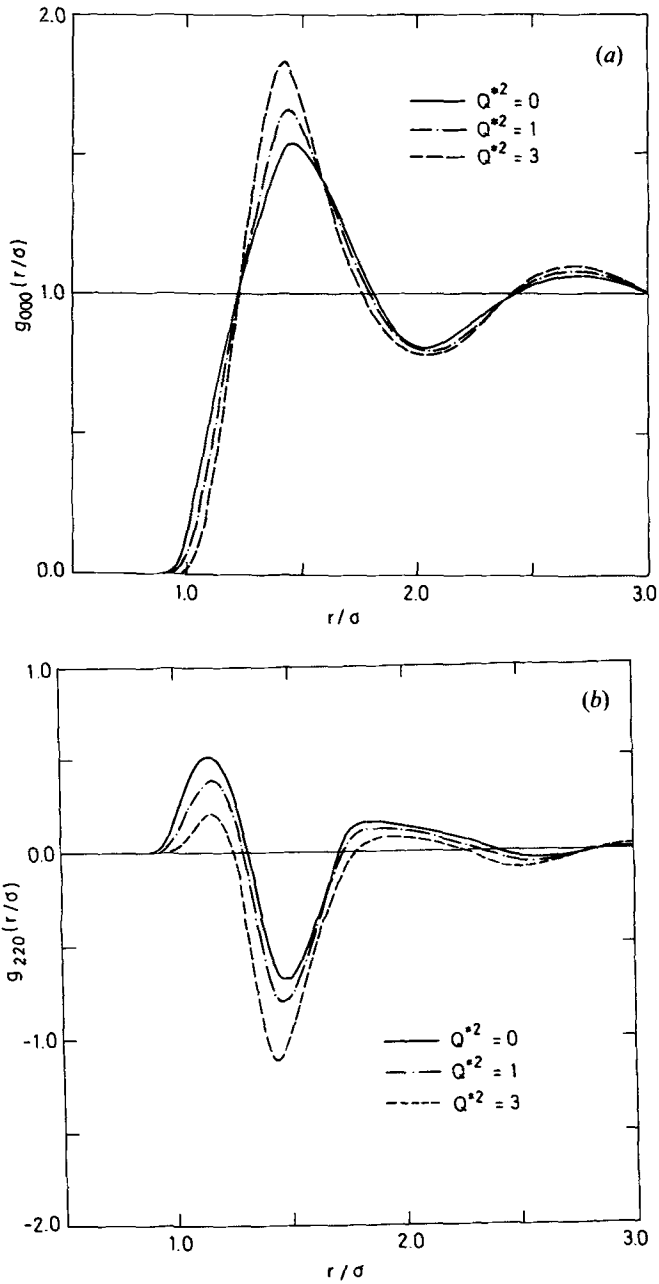


Figure 5. Spherical harmonic coefficients  $g_{l_1 l_2 m}(r)$  for the KQ model and  $L^* = 0.8118$ ,  $T^* = 1.50$ ,  $n^* = 0.36$ . Solid line  $Q^{*2} = 0$ , dot-dashed line  $Q^{*2} = 1$  and dashed line  $Q^{*2} = 3$ . (a)  $g_{000}(r)$ , (b)  $g_{220}(r)$ .

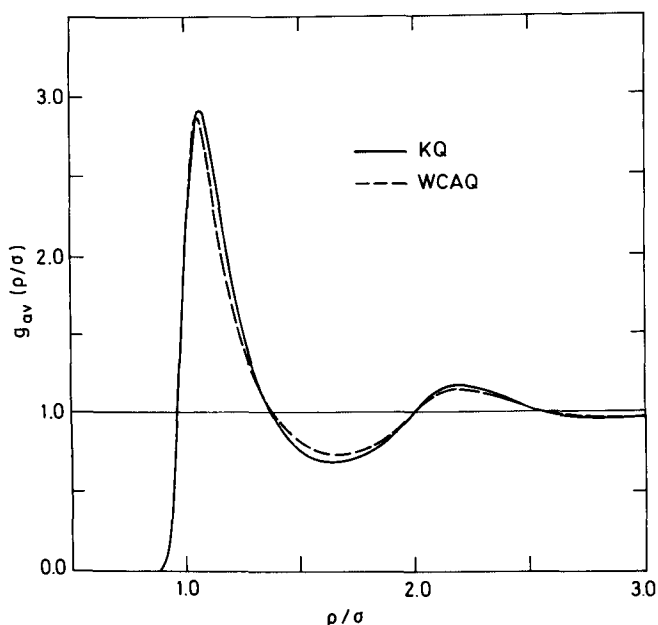


Figure 6. The surface-to-surface average correlation function  $g_{av}(\rho)$  (10) for  $L^* = 0.8118$ ,  $T^* = 1.10$ ,  $n^* = 0.36$ ,  $Q^{*2} = 3$ . Solid line KQ model and dashed line WCAQ model.

model. All the models underestimate the experimental value of  $Q$  in  $\text{CO}_2$  which is [44]  $Q = -4.0 \cdot 10^{-26}$  esu. We shall return to this point later. The value of  $\sigma$  for PS1–PS4 remains almost unchanged so that the volume of the molecule remains nearly constant. As the value of  $Q^{*2}$  increases, the value of  $\epsilon$  decreases so that the internal energy remains constant. Similar behaviour was found in a recent attempt to find potential parameters of a real dipolar molecule [39]. To decide between these models we did several runs for liquid state conditions and compared with the experimental results. The results for  $Q^{*2} = 0, 1.5, 2.5$  are shown in table 5. We do not include the results for  $Q^{*2} = 3.5$  because they did not improve the description. From table 5 we see that PS3 is the best model. As the temperature of the triple point [45] of  $\text{CO}_2$  is  $T_t = 217$  K, and the critical temperature is  $T_c = 304$  K, the results presented correspond to two subcritical isotherms and a supercritical one. For the two subcritical isotherms the smallest density corresponds to a point close to the orthobaric density. We have also included in table 5 the results of a more sophisticated model of  $\text{CO}_2$  [46]. First, by comparing the results of PS1 and PS3 we see that in fact, the inclusion of the quadrupole improves the description of  $\text{CO}_2$ . Second, we see that the agreement between the simulated (PS3) and the experimental results is good, and not significantly worse than the results of a more sophisticated model. In passing let us point out that recent simulation data for a 2CLJQ model of  $\text{CO}_2$  have been obtained [47] showing also good agreement with experimental results.

The value  $Q = -3.53 \cdot 10^{-26}$  esu (PS3) is smaller than the experimental one. An explanation for this could be that we are using a point quadrupole instead of a more realistic discrete charge quadrupole model. Lombardero *et al.* [25] have shown that for the HDQ fluid with  $L^* = 0.60$  the differences between ideal quadrupole and point charge quadrupole can be important at high densities and at large values of the quadrupole. Furthermore, a point quadrupole always gives a more negative quadru-

Table 3. MC results used to get the potential parameters of CO<sub>2</sub> modelled with the KQ pair potential with  $L^* = 0.8118$ .

$Q^{*2}$	$n^*$	$T^*$	$U/NkT$	$U^Q/NkT$	$Z$
0	0.325	0.7333	-5.885	0	0.022
0	0.325	0.75	-5.738	0	0.152
0	0.35	0.65	-7.296	0	-0.050
0	0.35	0.70	-6.711	0	0.396
1.5	0.30	0.85	-5.118	-0.597	-0.059
1.5	0.30	1	-4.191	-0.453	0.706
1.5	0.325	0.80	-5.994	-0.732	-0.054
1.5	0.325	0.85	-5.569	-0.667	0.294
1.5	0.35	0.70	-7.606	-1.009	-0.402
1.5	0.35	0.75	-6.994	-0.894	0.057
2.5	0.325	0.90	-5.983	-1.468	-0.016
2.5	0.325	0.95	-5.600	-1.3608	0.342
2.5	0.3425	0.855	-6.761	-1.712	-0.053
2.5	0.3425	0.875	-6.553	-1.654	0.122
2.5	0.36	0.85	-7.184	-1.862	0.406
2.5	0.36	0.90	-6.655	-1.67	0.851
2.5	0.36	0.95	-6.238	-1.546	1.124
2.5	0.36	1	-5.834	-1.431	1.557
3.5	0.3425	0.9833	-6.616	-2.423	0.004
3.5	0.3425	1.05	-6.046	-2.174	0.530
3.5	0.36	0.9333	-7.449	-2.784	0.046
3.5	0.36	1	-6.811	-2.508	0.566

polar energy than the point charge model, so that one needs a smaller value of the point quadrupole to fit the results of the internal energy for a point charge quadrupole. The same deviations were found for the HGOQ with point quadrupole and the HGO with discrete charge model, supporting this argument [48].

We can conclude that the PS3 KQ model yields a reasonable description of the liquid behaviour of CO<sub>2</sub>. To check whether we could also obtain a good description of the gas phase behaviour, we evaluated the second virial coefficient  $B_2$  for the models PS1 PS2 and PS3. The second virial coefficient is given by

$$B_2 = -2\pi \int (\langle \exp(-u/kT) \rangle - 1)r^2 dr, \quad (20)$$

where the brackets  $\langle \rangle$  stand for an unweighted average over the relative orientations. We evaluated the average using the Conroy [49] integration method with  $n = 4822$  orientations. The results, along with experimental values are shown in table 6. We see that the agreement is not good, and the worst is for the PS3 model. It is, therefore,

Table 4. Potential parameters of CO<sub>2</sub> obtained from the results of table 3.  $L^* = 0.8118$ .

Parameter set	$Q^{*2}$	$(\epsilon/k)/K$	$\sigma/\text{\AA}$	$Q 10^{-26}$ esu
PS1	0	340	2.815	0
PS2	1.5	304.5	2.82	-2.85
PS3	2.5	271	2.82	-3.48
PS4	3.5	239	2.8275	-3.89

Table 5. Comparison between the MC results for the KQ model of CO<sub>2</sub> with experimental values [43].

T/K	density/mol l <sup>-1</sup>	U/KJ/mol <sup>-1</sup>						p/bar					
		Exp.	PS1	PS2	PS3	[46]	Exp.	PS1	PS2	PS3	[46]		
230	25.68	-13.24	-13.13	-13.15	-13.19	-13.19	12	25	23	16	44		
230	27.71	-14.26	-14.22	-14.25	-14.35	-14.18	504	635	620	462	529		
270	21.78	-10.86	-10.82	-10.73	-10.66	-10.83	50	-37	46	77	32		
270	27.09	-13.42	-13.58	-13.45	-13.42	-13.30	1003	1112	1143	1051	999		
350	5.20	-2.85	-2.75	-2.65	-2.58	-2.84	100	94	103	109	100		
350	23.36	-10.68	-11.16	-10.87	-10.64	-10.78	1002	1005	1083	1120	1017		

Table 6. Second virial coefficient of CO<sub>2</sub> from experiment [43], and as estimated from the KQ model with the potential parameters of table 4.

T/K	$B_2(T)/\text{cm}^3 \text{mol}^{-1}$			
	Exp.	PS1	PS2	PS3
210	*	-247	-235	-229
250	-184.5	-174	-162	-154
300	-122.7	-120	-109	-100
400	-60.5	-63	-54	-47
600	-12.1	-15	-9	-4

clear that a good description of both the liquid and gas phases cannot simultaneously be achieved with the KQ model. The PS3 model must be regarded as an effective pair potential for the liquid phase. Similar conclusions were obtained for other potential models when the potential parameters were fitted to liquid state properties [50].

In conclusion we can say that the KQ model gives a reasonable description of CO<sub>2</sub> in the liquid state for internal energy and pressure, and can be regarded as a simple effective pair potential of CO<sub>2</sub>; however, a simultaneous description of the liquid and gas phases can not be achieved with this model.

### 5. Conclusions

In this work we have carried out MC simulations of the Kihara model with an embedded point quadrupole. From the simulations we have obtained the contribution of the quadrupole to the Helmholtz free energy  $A_Q$ . Since this is the property typically obtained in theoretical treatments, the data should be useful to test theoretical approaches. The quadrupole modifies the structure of the fluid, the changes being similar to those observed in the HDQ and in 2CLJQ models. The function  $g_{av}(\rho)$  is not, however, much affected by the quadrupole. We have observed that  $A^Q$  is very similar for the KQ fluid and WCAQ fluids. Further theoretical work on purely repulsive quadrupolar fluids is therefore needed.

Finally, we have shown that the KQ model provides a good effective pair potential for CO<sub>2</sub> in the liquid phase, although it is not able to reproduce simultaneously the thermodynamic behaviour in gas and liquid phases. The description of CO<sub>2</sub> with the Kihara potential model is improved when a point quadrupole is included.

One of us (C.V.) would like to thank the Plan de Formacion del Personal Investigador of Spain for a grant, and the hospitality at Cornell University during his visit. We thank the Department of Energy, Division of Basic Chemical Sciences, for a grant in support of this research.

### References

- [1] WEEKS, J. D., CHANDLER, D., and ANDERSEN, H. C., 1971, *J. chem. Phys.*, **54**, 5232.
- [2] TILDESLEY, D., 1980, *Molec. Phys.*, **41**, 341.
- [3] LOMBARDEO, M., ABASCAL, J. L. F., and LAGO, S., 1981, *Molec. Phys.*, **42**, 999.
- [4] MCGUIGAN, D. B., LUPKOWSKI, M., PAQUET, D. M., and MONSON, P. A., 1989, *Molec. Phys.*, **67**, 33.
- [5] KOHLER, F., QUIRKE, N., and PERRAM, J., 1979, *J. chem. Phys.*, **71**, 4128.
- [6] FISCHER, J., 1980, *J. chem. Phys.*, **72**, 5371.
- [7] FISCHER, J., and LAGO, S., 1983, *J. chem. Phys.*, **78**, 5750.

- [8] LUSTIG, R., 1986, *Molec. Phys.*, **59**, 173.
- [9] LADO, F., 1982, *Molec. Phys.*, **47**, 283.
- [10] MONSON, P. A., and GUBBINS, K. E., 1983, *J. phys. Chem.*, **87**, 2852.
- [11] MONSON, P. A., and GUBBINS, K. E., 1983, *Fluid Phase Equil.*, **13**, 161.
- [12] BOUBLIK, T., 1989, *Molec. Phys.*, **67**, 1327.
- [13] SEDIAWAN, W. B., GUPTA, S., and McLAUGHLIN, E., 1987, *Molec. Phys.*, **62**, 141.
- [14] BERNE, B. J., and PECHUKAS, P., 1972, *J. chem. Phys.*, **56**, 4213.
- [15] KIHARA, T., 1951, *J. phys. soc. Japan*, **16**, 289.
- [16] BOUBLIK, T., 1987, *J. chem. Phys.*, **87**, 1751.
- [17] PADILLA, P., and LAGO, S., 1989, *Fluid Phase Equil.*, **48**, 53.
- [18] VEGA, C., and LAGO, S., 1991, *J. chem. Phys.*, **94**, 310.
- [19] GRAY, C. G., and GUBBINS, K. E., 1984, *Theory of Molecular Fluids*, Vol. I (Clarendon).
- [20] BOHN, M., FISCHER, J., and HAILE, J., 1988, *Molec. Phys.*, **65**, 797.
- [21] CHEUNG, P. S. Y., and POWLES, J. G., 1976, *Molec. Phys.*, **32**, 1383.
- [22] AGRAVAL, R., SANDLER, S. I., and NARTEN, A. H., 1978, *Molec. Phys.*, **35**, 1087.
- [23] STREETT, W. B., and TILDESLEY, D. J., 1977, *Proc. R. Soc. A.*, **355**, 239.
- [24] WOJCIK, M. C., and GUBBINS, K. E., 1984, *J. phys. Chem.*, **88**, 6559.
- [25] LOMBARDO, M., MARTIN, C., LOMBA, E., and ABASCAL, J. L. F., 1989, *J. phys. Chem.*, **93**, 4636.
- [26] WOJCIK, M. C., and GUBBINS, K. E., 1984, *Molec. Phys.*, **51**, 951.
- [27] BOUBLIK, T., VEGA, C., LAGO, S., and PENA, M. D., 1990, *Molec. Phys.*, **71**, 1193.
- [28] BOUBLIK, T., 1991, *Molec. Phys.*, **73**, 419.
- [29] SEVILLA, P., and LAGO, S., 1985, *Comput. Chem.*, **9**, 39; LAGO, S., and VEGA, C., 1988, *Comput. Chem.*, **12**, 343.
- [30] METROPOLIS, N., ROSENBLUTH, A. W., ROSENBLUTH, M. N., TELLER, A. H., and TELLER, E., 1953, *J. chem. Phys.*, **21**, 1087.
- [31] EPPENGA, R. E., and FRENKEL, D., 1984, *Molec. Phys.*, **52**, 1303.
- [32] VEGA, C., and FRENKEL, D., 1989, *Molec. Phys.*, **67**, 633.
- [33] KANTOR, R., and BOUBLIK, T., 1988, *Czech. J. Phys.*, **B38**, 321.
- [34] KANTOR, R., and BOUBLIK, T., 1989, *Molec. Sim.*, **2**, 217.
- [35] BOUBLIK, T., and NEZBEDA, I., 1986, *Coll. Czech. Chem. Commun.*, **51**, 2301.
- [36] KIRKWOOD, J. G., 1935, *J. chem. Phys.*, **3**, 300.
- [37] PATEY, G. N., and VALLEAU, J. P., 1976, *J. chem. Phys.*, **64**, 170.
- [38] VEGA, C., and LAGO, S., 1991, *Molec. Phys.*, **72**, 215.
- [39] VEGA, C., SAAGER, B., and FISCHER, J., 1989, *Molec. Phys.*, **68**, 1079.
- [40] KIHARA, T., 1975, *Adv. chem. Phys.*, **33**, 51.
- [41] FISCHER, J., LUSTIG, R., BREITENFELDER-MANSKE, H., and LEMMING, W., 1984, *Molec. Phys.*, **52**, 485.
- [42] WOJCIK, M., GUBBINS, K. E., and POWLES, J. G., 1982, *Molec. Phys.*, **45**, 1209.
- [43] ANGUS, S., ARMSTRONG, B., and DE REUCK, K. S., 1873, *International Thermodynamics Tables of the fluid state*, Vol. 3, *Carbon dioxide* (Pergamon).
- [44] GRAHAM, C., PIERRUS, J., and RAAB, R. E., 1989, *Molec. Phys.*, **67**, 939.
- [45] DUSCHEK, W., KLEINRAHM, R., and WAGNER, W., 1990, *J. chem. Ther.*, **22**, 841.
- [46] LUCKAS, M., and LUCAS, K., 1989, *Fluid Phase Equil.*, **45**, 7.
- [47] MOLLER, D., 1991, PhD Thesis Dissertation, Ruhr-Universitat, Bochum.
- [48] VEGA, C., and BOUBLIK, T., Unpublished results.
- [49] CONROY, H., 1967, *J. chem. Phys.*, **47**, 5307.
- [50] VEGA, C., and LAGO, S., 1990, *J. chem. Phys.*, **93**, 8171.