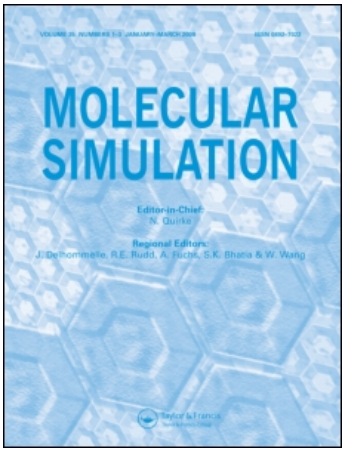

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On the Possibility of Finding a Suitable Potential Model For Liquid CO_2

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Preliminary Communication

ON THE POSSIBILITY OF FINDING A SUITABLE POTENTIAL MODEL FOR LIQUID CO_2

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The behaviour of the lower harmonic coefficients of the liquid state angular correlation function of CO_2 has been studied using theory and simulation.

KEY WORDS: Liquid CO_2, molecular dynamics, y-expansion

Computer modelling of molecular liquids is still a challenging problem. In particular, liquids composed of linear molecules have been the subject of several investigations [1, 2, 3, 4], and the comparison with X-ray and neutron scattering diffraction data has provided a suitable test of the reliability of the proposed models. In fact, the measurements of the partial structure factors give information on the atom–atom distribution functions, but not directly on the orientational order set up in the liquid phase. Raman spectra are also sensitive to the angular correlations between pairs of molecules: for a realistic interpretation of the experimental data it has been demonstrated that interaction induced effects changing the polarizability of a molecule, have to be taken into account [5], and the dipole-induced-dipole (DID) mechanism is found to give the overwhelming contribution to the scattered intensity. For linear molecules, the effective Raman polarizability can be written in terms of parameters introduced by Ladanyi and Keyes [6], τ_{20} and τ_{22} which are expressed in terms of particular spherical components of the pair radial distribution function, namely;

$$\tau_{20} = 4\pi \int_0^\infty g_{200}(r)\, dr/r \tag{1}$$

$$\tau_{22} = 4\pi \int_0^\infty [2g_{222}(r) - g_{220}(r) + g_{221}(r)]\, dr/r \tag{2}$$

where the $g_{ll'm}$ (r) are implicitly defined by [7]

$$g(1, 2) = 4\pi \Sigma_{ll'm} g_{ll'm}(r)\, Y_l^m(\Omega_1)\, Y_{l'}^{-m}(\Omega_2). \tag{3}$$

The τ parameters are sensitive to the change of the spherical component behaviour when different interaction potential models are used [8].

From a computational point of view it would be convenient to rely on some perturbation scheme which allows one to derive the $g_{ll'm}(r)$ components in terms of a single (and possible simpler) quantity. Such perturbation expansions have been developed [9] and the so called "y-expansion" has been found to reproduce better the computer simulation results for moderately anisotropic systems modelling Br_2 [10]. In essence the y-expansion assumes that the structure of the fluid is determined by an effective two-body potential $u_0(r)$ obtained by an angular average of the model potential $u(1, 2)$ over the orientation of the molecules: i.e.

$$\exp[-\beta u_0(r)] = < \exp[-\beta u(1,2)] >_{\Omega_1, \Omega_2}$$

The centre of mass distribution function is obtained by computer simulation of a reference "monatomic" system at the desired temperature and density where the particles interact through the potential $u_0(r)$. The spherical harmonic components

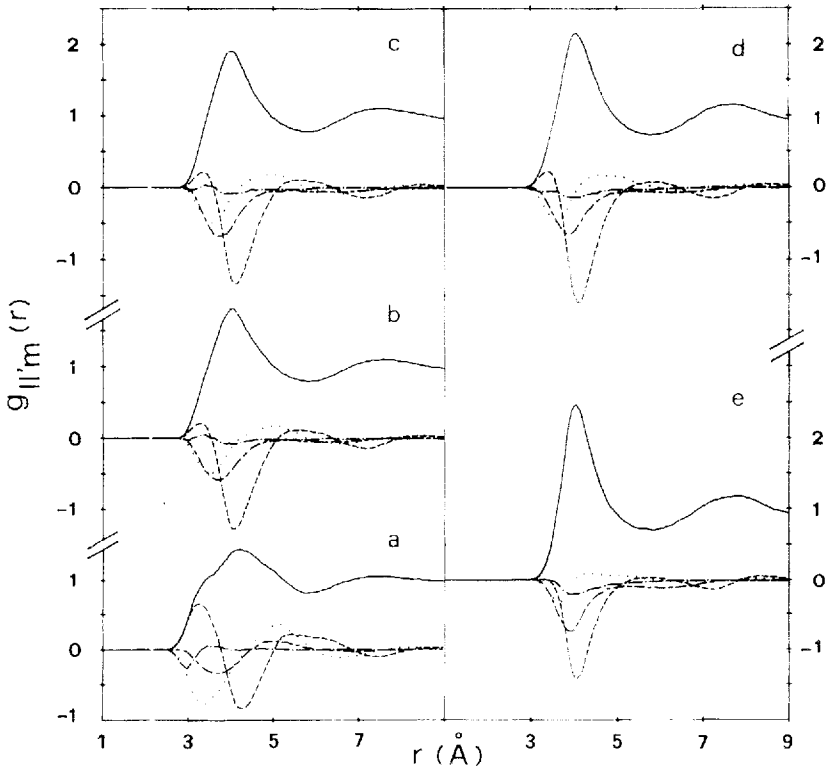

Figure 1 The first spherical harmonic coefficients for the investigated potentials. The labels are: (a) for the potential 2CLJ of reference 1; (b) for 2CLJQ (potential A1 of reference 11); (c) for 3CLJQ [11]; (d) and (e) for the potentials of reference 13 with a quadrupole moment equal to -4.49 DÅ (experimental value) and -5.8 DÅ respectively. Solid lines correspond to g_{000}; dotted lines to g_{200}; dashed lines to g_{220}; dashed-dashed to g_{221}; dashed-dotted to $g_{\ldots}$.

$g_{ll'm}(r)$ which appear in the expansion (3), are then given in the zero order approximation by [10]:

$$g_{ll'm}(r) = g_0(r) \exp[\beta u_0(r)]\, {}^{(0)}g_{ll'm}(r)$$

where ${}^{(0)}g_{ll'm}$ represents the spherical harmonic coefficients calculated in the low density limit, i.e. when we use $g(1,2) = \exp[-\beta u(1,2)]$ corresponding to an evaluation performed with only two molecules.

We have analyzed the behaviour of the first harmonic components for different potential models proposed for CO_2, i.e. a two Lennard-Jones centre (2CLJ) model [1], 2CLJ plus a point quadrupole interaction (2CLJQ) [11], a three centre plus quadrupole (3CLJQ) and two models implemented by Böhm et al. [12, 13]. The aim of this investigation is twofold: first to compare the different orientational order induced by different potentials, second to analyze to what extent the perturbation scheme can account for the various spherical harmonics for such an anisotropic system. The probability of occurrence of particular configurations has been calculated in order to have a more complete view of the structure of the liquid and to supplement the study of the atom-atom distribution function already performed in connection with the neutron scattering data [14, 15].

In figure 1 we present the results for various spherical harmonic components obtained by molecular dynamics (MD) simulations of liquid CO_2 at $T = 222$ K and $\varrho = 1.15$ g/cm^3. The MD runs have been performed with 256 particles in the same

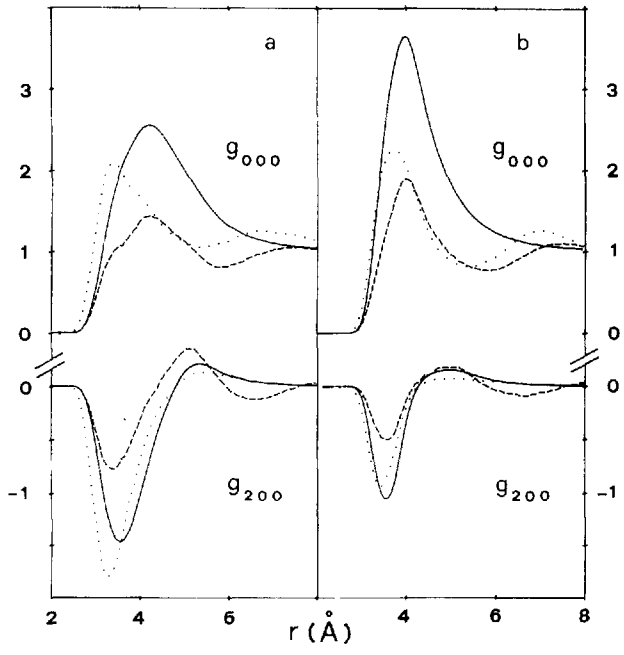

Figure 2 Spherical harmonic components g_{000} and g_{200} for 2CLJ (a) and 3CLJQ (b) potentials, calculated in the low density limit approximation (solid line), in the zero-order γ-expansion (dotted line) and by MD simulations (dashed line).

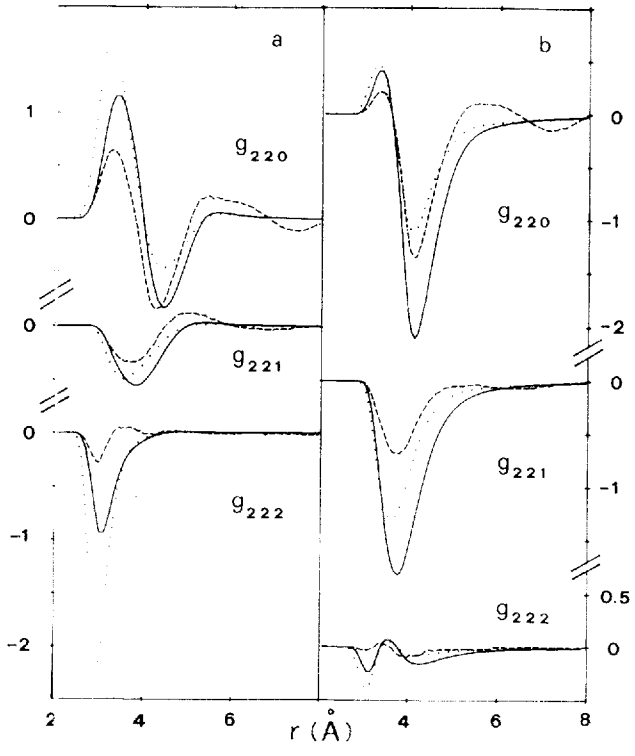

Figure 3 The same as in Figure 2, but for g_{220}, g_{221} and g_{222}.

way as discussed in reference 15 and the averages have been calculated over 6,000 time steps. It is evident that there are large differences among the various potential models, as already expected from the behaviour of the atom–atom distribution functions. A detailed discussion will be presented elsewhere. At present we want to stress that the Böhm's model [13] which reproduces the experimental quadrupole moment, differs negligibly from 3CLJQ, and that for this system the use of distributed charges instead of a point quadrupole has little influence on the overall behaviour. Therefore we shall focus our attention on the comparison between only two models, namely the 2CLJ and 3CLJQ.

For these two potentials we present in figures 2 and 3 the first spherical harmonic coefficients compared with those calculated in the zero order y-expansion and in the low density limit. It appears that the main features are already present in the low density limit results, the major differences being due to a packing effect which reduces the orientational correlations at short distances, but induces evident correlations beyond the first shell of neighbours. The modifications introduced by the packing effect through the centre–centre distribution function in the zero order y-expansion do not improve the behaviour around the second shell distances and lead to better agreement with the MD results at short distances only for the 3CLJQ model. The lack of improvement for the 2CLJ model can be attributed to the very high anisotropy of this potential in the region of the first shell.

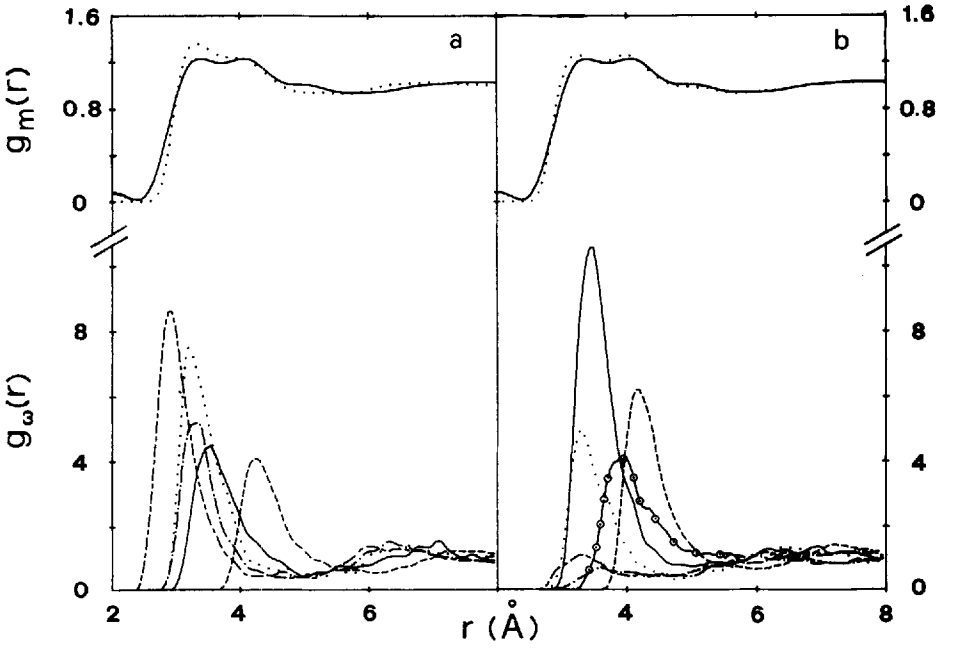

Figure 4 Radial distribution function $g_m(r)$ as probed by neutron scattering (solid lines at the top) together with MD (dotted lines) using the 2CLJ (part a) and 3CLJQ (part b) potentials. The curves at the bottom are the probability distributions for particular configurations: T-shaped (dashed line); Crossed (dashed-dashed line); Parallel (dashed-dotted line); Canted-Parallel at 70° (dotted), 60° (solid) and 50° (solid line with open circles).

The changes of the spherical harmonic coefficients by adopting different potentials are strongly reflected on the values of τ_{20} and τ_{22}, which are found to be -4.52 and 9.88 for 2CLJ respectively, while for 3CLJQ they are -2.35 and 3.69.

Finally, in figure 4 we report the distribution of standard configurations [1, 2, 13] together with the experimental (from neutron scattering) and MD radial distribution function. From the figure one can infer that the better agreement of the 3CLJQ potential is due to the strong reduction of cross and parallel configurations and to the enhancement of T-shaped ones.

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