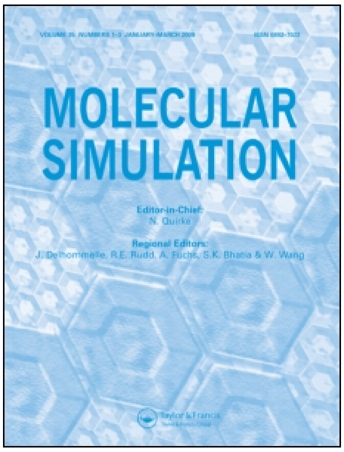

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On the Uniqueness of the Reverse Monte Carlo Simulation for Molecular Liquids

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ON THE UNIQUENESS OF THE REVERSE MONTE CARLO SIMULATION FOR MOLECULAR LIQUIDS

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A careful analysis of the three dimensional structures of liquid Chlorine produced by the Reverse Monte Carlo (RMC) and Molecular Dynamics (MD) techniques is presented. The analysis allows us to measure the degree of uniqueness between the potential and the atom-atom distribution functions, $g_{aa}(r)$, in the case of pairwise potentials formed by isotropic and anisotropic site-site interactions. The $g_{aa}(r)$ obtained from MD simulations are used as 'experimental' input data in the RMC procedure and the constraint of rigid molecules is imposed. The particle configurations produced by RMC are then studied by using a recently proposed general method for analysing the local order in liquids. The same analysis applied to the particle configurations produced by the conventional MD simulation yields a set of partial distribution functions which relates the main features of the $g_{aa}(r)$ to microscopic pair geometries. The comparison between the partial centre-centre $g_{cc}(r)$ shows that the three dimensional structures, produced by MD and RMC simulations, agree very well when only isotropic site-site interactions act. In this case RMC produces the same radial distribution function $g(r, \omega_1, \omega_2)$ as that obtained from the original MD configurations; it is therefore a valid tool for deriving a complete information on the physical properties of a fluid. For anisotropic site-site interactions the partial $g_{cc}(r)$ of MD and RMC differ significantly and show that the three dimensional structures, produced by MD and RMC simulations, differ too. The discrepancies are particularly evident for the T shaped configurations and affect the values of the potential energy. Therefore, even if the potential is purely pairwise additive, the use of the atomic radial distribution function as input data and the imposition of atomic constraints which model the molecules as hard dumbbells are not sufficient to bring the RMC procedure towards the 'true' microscopic structure of the liquid; the presence of non central forces between sites disrupts the bijective correspondence between the potential and the $g_{aa}(r)$.

KEY WORDS: Structure of liquids, reverse monte carlo, molecular dynamics, local order in liquids, uniqueness theorem for the pair correlation functions.

1 INTRODUCTION

The Reverse Monte Carlo (RMC) simulation has become a widely used tool for analysing the structure of simple and complex liquids. Originally, it was proposed by McGreevy and Pusztai [1] for deriving three dimensional microscopic structures of monatomic systems by experimental data without the use of interatomic potential models. Indeed, the RMC technique uses the measured structure factor or, equivalently, the radial distribution function $g(r)$, as experimental input data and produces a three dimensional structural model consistent with the experimental input. The major problem which has been often raised about the validity of the RMC method for structural analysis was that of the uniqueness of the produced structural models [2, 3]. For monoatomic systems, the uniqueness theorem for the pair correlation function $g(r)$ [2, 3] establishes a one-to-one correspondence between the potential and the $g(r)$, provided pairwise interactions act. In such a case, all the higher order correlation functions are uniquely determined; then, the RMC technique is a valid tool for deriving further structural information from the produced set of particle configurations, such as three-body correlation functions and bond angle distributions [4–6].

For molecular liquids the problem is more complicated since the structure is determined by the intermolecular centres of mass distance, r, as well as by the angular sets ω_1 and ω_2 defining the molecular orientations. In the limit of pairwise interactions, the uniqueness theorem establishes a one-to-one relation between the potential and the orientational radial distribution function $g(r, \omega_1, \omega_2)$ [2]. But $g(r, \omega_1, \omega_2)$ cannot be derived directly by experiments which provide the site-site pair correlation functions $g_{\alpha\beta}(r)$. As is well known, $g_{\alpha\beta}(r)$ contains in general an irreversible lack of structural information with respect to $g(r, \omega_1, \omega_2)$. Only if an isotropic site-site potential acts (*i.e.* the forces between sites are central and depend on the site-site scalar distance $r_{\alpha\beta}$ only), there is a one-to-one correspondence between $g_{\alpha\beta}(r)$ and the potential and, consequently, between $g_{\alpha\beta}(r)$ and $g(r, \omega_1, \omega_2)$. So, in contrast with the atomic case, we cannot provides the RMC procedure with the experimental input data which are needed for determining a realistic three dimensional structure in the pairwise potential approximation. Molecular dynamics (MD) simulations have shown that for many systems, even as simple as diatomic liquids, non central forces play a relevant role; together with central interactions, *e.g.* the Lennnard-Jones (LJ) ones, anisotropic forces, like quadrupolar and dipolar ones, are necessary for reproducing the experimental $g_{\alpha\beta}(r)$, correctly. In this case, the one-to-one correspondence between $g_{\alpha\beta}(r)$ and $g(r, \omega_1, \omega_2)$ breaks down and the validity of the RMC method is doubtful. In contrast with the case of monatomic systems, the reliability of the structural models of molecular systems produced by RMC simulations have been very little investigated. This is probably due to the difficulty of exploring all the phase space which the $g(r, \omega_1, \omega_2)$ spans. The only study in this sense is due to McGreevy and Howe [5]; the results are however uncertain because only few coefficients of the harmonic expansion of $g(r, \omega_1, \omega_2)$ have been tested and, in the case of non central forces, input data obtained by a small size simulation box have been used.

In this work we present a careful analysis of three dimensional structure produced by a RMC procedure which uses, as particle that can be moved, molecular units rather than atoms. The input data of RMC will be the $g_{\alpha\beta}(r)$ obtained from molecular configurations produced by MD simulations. Our aim is to clarify the following points:

a) In the case of isotropic site-site interactions, the set of $g_{\alpha\beta}(r)$ could be sufficient to determine uniquely the structure of a liquid. If we use such functions as input data of the RMC procedure, the produced RMC configurations and the original MD configurations would provide the same $g(r, \omega_1, \omega_2)$. Then the RMC is a valid tool for deriving structural information, such as the orientational pair correlation functions and higher order correlations, which are not derivable from the one dimensional functions $g_{\alpha\beta}(r)$.

b) If the test a) is successful, the same analysis can be extended to systems for which the potential is purely pairwise additive but it is formed by non central forces. In this case there is no theoretical justification for the determination of the three dimensional structure from the one dimensional set of $g_{\alpha\beta}(r)$. If the $g(r, \omega_1, \omega_2)$ obtained from RMC and MD configurations coincide then the RMC yield structural information beyond that contained in $g_{\alpha\beta}(r)$. In other words, the dependence of $g_{\alpha\beta}(r)$ upon non central forces is sufficient to determine accurate structural information.

The main difficulty in performing such tests appears to be the problem of comparing two functions $g(r, \omega_1, \omega_2)$ for every value of ω_1 and ω_2. In principle, this can be done by expanding $g(r, \omega_1, \omega_2)$ in an infinite series of spherical harmonics; but careful studies [7] have shown that the series converges slowly and there are serious problems of statistical errors; in the case of simple diatomic liquids, about 16 terms need to obtain quantitative estimate of $g(r, \omega_1, \omega_2)$. Alternatively, it is possible to use the following method of analysis of the orientational order [8]: the total $g(r)$ is decomposed in a finite set of microscopic configurations Γ which represent classes of distorted dimer geometries, that is $g(r) = \Sigma_\Gamma\, g^\Gamma(r)$. In the case of diatomic molecules, a set of five disjoint classes is sufficient to complete the total angular space and to reproduce the main features of the $g(r)$. In practice, $g^\Gamma(r)$ are angular average of $g(r, \omega_1, \omega_2)$ within the angular limits of a configuration. Then, to compare two $g(r, \omega_1, \omega_2)$ we will proceed as follows: the radial distribution functions $g_{\alpha\beta}(r)$, resulting from a conventional MD simulation which exploits pairwise additive potential, are used as experimental input in the RMC procedure; from the particle configurations which are generated, each $g^\Gamma(r)$ is computed and then compared with the same function obtained by conventional simulation. If they agree, the angular limits which define the configuration Γ can be decreased, the comparison repeated and so on. When the comparison is repeated for all the configurations Γ, all the angular phase space of a pair has been sampled. If the agreement is always found, the two $g(r, \omega_1, \omega_2)$ coincide and the RMC procedure yields a three dimensional structure equal to the original one produced by MD.

Recently the RMC procedure for atomic liquids has been extended to molecular liquids, namely to the diatomics [9], water [10] and Acetonitrile [11]. For obvious reasons of simplicity, in this work we will use some models of linear molecules for testing the RMC; this makes more simple the study of the angular space of a pair which depends upon three polar angles only. The liquid chlorine is particularly suitable for this study, since four effective potential models have been developed. The two centres Lennard-Jones (LJ) model [12] is formed by purely central atom-atom interactions and allows to perform the test a) In the LJQ potential model [13], the central atomic interactions are implemented by non central forces between point quadrupole placed over the centres of mass of the molecules. Finally, the A2 [14] and WP [15] models are formed by anisotropic site-site interactions. These last three models allows to perform the test b) for determining if the RMC procedure 'see' the non site-site interactions present over the $g_{\alpha\beta}(r)$, uniquely; in other words, while $g_{\alpha\beta}(r)$ certainly depends upon the non central interactions (which are present together with the central ones in the potential models), this dependence could be insufficient to determine uniquely the interactions themselves.

2 THE MD AND RMC SIMULATIONS

For homonuclear diatomic molecules, the LJ potential models the repulsive and the attractive dispersion forces with the following well known expression

$$V=\sum_{\alpha,\beta}4\varepsilon\left[\left(\frac{\sigma}{r_{\alpha\beta}}\right)^{12}-\left(\frac{\sigma}{r_{\alpha\beta}}\right)^{6}\right] \tag{1}$$

The sites α, β coincide with the atoms of the molecule. The values of the parameters which fits the liquid chlorine are due to Singer *et al.* [12]. Equation (1) shows that the potential only depends upon the scalar distance $r_{\alpha\beta}$ so that the interactions between atoms are central. This potential yields a radial distribution function $g_{\alpha\beta}(r)$ which disagrees with the experimental one. For this reason, Murthy *et al.* [13] have implemented the LJ potential with the lowest order electrostatic multipole-multipole interaction by placing a point quadrupole moment, Q_2, at the molecular centre; the explicit form of the electrostatic potential energy is:

$$V_{es}=\frac{6}{4\pi\varepsilon_0}Q_2{}^2S_{224}r^{-5} \tag{2}$$

where S_{l_1,l_2j} stands for the spherical harmonic function [14]; the dependence of S_{l_1,l_2j} on the molecular orientations makes the interaction non central. To explain certain features of the crystalline and liquid phase of the halogens, Rodger *et al.* [14] have introduced a very sophisticated potential model, usually referred to as A2 potential. This potential, written as $V=V_{rep}+V_{disp}+V_{es}$, has the following functional form

$$V_{rep}=K_0\exp\{-a[r_{\alpha\beta}-\sigma(\Omega_{12})]\} \tag{3}$$

$$\sigma(\Omega_{12})=\sigma_0+\sigma_1S_{110}+\sigma_2(S_{202}+S_{022})+\sigma_3(S_{303}+S_{033}) \tag{4}$$

$$V_{disp}=-C[r_{\alpha\beta}+\xi_0-\sigma(\Omega_{12})]^{-6} \tag{5}$$

$$V_{es}=\frac{1}{4\pi\varepsilon_0}[2Q_1{}^2S_{112}r_{\alpha\beta}^{-3}+3Q_1Q_2(S_{123}+S_{213})r_{\alpha\beta}^{-4}+6Q_2{}^2S_{224}r_{\alpha\beta}^{-5}] \tag{6}$$

As is seen, the repulsive, V_{rep}, and dispersive, V_{disp}, parts of the potential are non central since they depend on the relative orientation Ω_{12} of two molecules via the spherical harmonic functions $S_{l_1 l_2 j}$ of Equation (4). Furthermore, Equation (6) shows that a point dipole Q_1 and a point quadrupole Q_2, placed over each atom, contribute to increase the anisotropy of the atomic sites. The last potential, proposed for modelling liquid chlorine, is due to Wheatly and Price (WP potential) [15]. This potential arises from the application of a systematic method based on calculations applied to the *ab initio* isolated monomer wave functions. The form of the electrostatic part is identical to that of A2. The functional form of the repulsive and dispersive parts is more complicated since, beyond the non central atom-atom interactions, anisotropic forces between molecular centre and peripheral atom are involved; in spite of this, it requires only four adjustable parameters, one half of that required by A2. We refer to the original work [15] for the analytical expressions and the parameter values of the WP potential.

The way in which forces and torques are computed in the MD program and the other details of the procedure used for producing particle configurations are reported in Ref. [16]. The atom-atom radial distribution function $g_{\alpha\beta}(r)$, obtained from MD simulation of liquid chlorine at the temperature of 200 K and molar volume of 4.26 10^{-5} m^3, are reported in Figure 2. It has been derived from 300 recorded configurations of 500 molecules; this ensures a statistical error, computed following the method described in Ref. [17], always smaller than 10^{-2}, this value affecting the region of the first peak of $g_{\alpha\beta}(r)$.

The RMC procedure exploited the code for the atomic system kindly provided us by McGreevy. The original version has been adapted to run over an IBM PowerPC and modified to keep fixed the molecular bond length at the values of each potential model. The closest distance of approach constraint is usually imposed to the atomic systems to forbid the overlap of atoms; in our case, the closest approach has been chosen equal to the values at which each MD $g_{\alpha\beta}(r)$ starts to be different from zero, that is 2.95 Å, 2.90 Å, 2.85 Å and 2.85 Å for LJ, LJQ, A2 and WP potentials, respectively. The RMC simulation was performed over a system of 500 molecules contained in a cubic box which dimension reproduced the molar volume of MD. The starting configuration was produced by choosing the centres of mass positions and the molecular orientations at random. New configurations, produced by displacing and rotating the molecules randomly, are accepted or rejected by using the usual RMC criterion [1]; that is, after each move, the quantity

$$\chi^2 = \sum_n [g_{\mathrm{aa}}^{\mathrm{MD}}(r_n) - g_{\mathrm{aa}}^{\mathrm{RMC}}(r_n)]^2 / \varepsilon^2$$

where ε stands for the experimental uncertainty, is computed and the move accepted if χ^2 decreased; otherwise it was accepted with probability $\exp[-\Delta\chi^2/2]$, $\Delta\chi^2$ being the χ^2 variation caused by the move. The maximum values allowed for each displacement was 0.1 Å and for each rotation 15° for both the polar angles; the constant value of ε has been fixed at 0.02, nearly equal to two times the maximum standard deviation of the statistical errors. The χ^2 values have been controlled until the equilibrium value, around which it fluctuates, has been reached. Then statistically independent configurations have been collected by recording at every 5000 accepted moves. For saving computing time, the χ^2 has been computed in the r-range of the first neighbours, 0–8 Å; as we shall see later, this is sufficient to determine agreement on the overall r-range.

3 RESULTS AND DISCUSSIONS

3.1 MD Simulation

Before considering the RMC procedure, it is worth discussing the results of the conventional MD simulation. Figure 1 shows the leading geometries giving rise to the five classes of distorted configurations Γ which fill the angular space of a pair; the angular limits which define the classes [8] are reported in Table 1. It must be noted that the LP class contains the geometries usually referred to as L, end-to-end and shifted parallel. It is also worth noting that the P and X are compact configurations since the centres of mass of the pair reach the smallest distance; by contrast the T and LP are elongated configurations while the V can be considered intermediate configurations. Figure 2 and 3 show the total and partial contributions to the $g(r)$ due to atoms and centres, respectively. As is seen in Figure 2, the first peak of the $g_{\alpha\beta}(r)$ is due to both compact and elongated configurations while only the elongated ones determine the shape of the second peak. It is also evident that the four potential yield quite different predictions. The addition of the anisotropic quadrupolar forces (LJQ) to the isotropic interactions (LJ) clearly favours the T configurations. This is however insufficient to determine a sharp second peak as the experimental data require [18]. As pointed out in Ref. [16], the anisotropic site-site

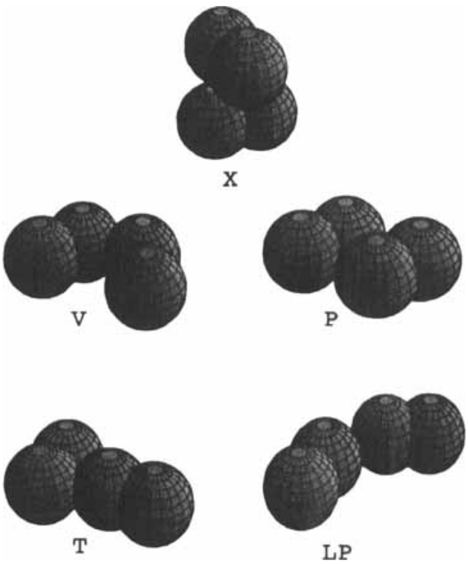

Figure 1 Leading geometries of the Cl_2 dimer. The molecule of Cl_2 is modelled by two spheres of diameter 3.64 Å and bond length of 1.98 Å.

Table 1 Values (in degree) of the polar angles specifying the dimer geometries of Figure 1 and of the angular tolerances specifying the configurations Γ. The angles θ_1 θ_2 and $\varphi = \varphi_1 - \varphi_2$ yield the orientations of the two intramolecular atom-atom vectors and are evaluated in an intramolecular frame in which the *z* axis lies along the intermolecular centres of mass distance. The values Ω^Γ of the related solid angle fractions are reported.

		$\Delta\Theta_1$	$\Delta\Theta_2$	$\Delta\varphi$	Ω^Γ
T	$\Theta_1 = 90$	± 40	± 50	$0-360$	.357
	$\Theta_2 = 0$	± 30	± 30	$0-360$	.134
		± 15	± 15	$0-360$	.0176
LP	$\Theta_1 = 30$	± 30	± 30	$0-360$	.25
	$\Theta_2 = 150$	± 15	± 15	$0-360$	.0670
		± 5	± 5	$0-360$	.00760
P	$\Theta_1 = 75$	± 15	± 20	± 60	.131
	$\Theta_2 = 70$	± 10	± 10	± 60	.0533
	$\varphi = 0$	± 5	± 5	± 60	.0159
X	$\Theta_1 = 90$	± 30	± 40	± 30	.131
	$\Theta_2 = 90$	± 25	± 25	± 25	.0496
	$\varphi = 90$	± 15	± 15	± 15	.0112
V	$\Theta_1 = 75$	± 15	± 20	± 60	.131
	$\Theta_2 = 110$	± 10	± 10	± 60	.0533
	$\varphi = 0$	± 5	± 5	± 60	.0159

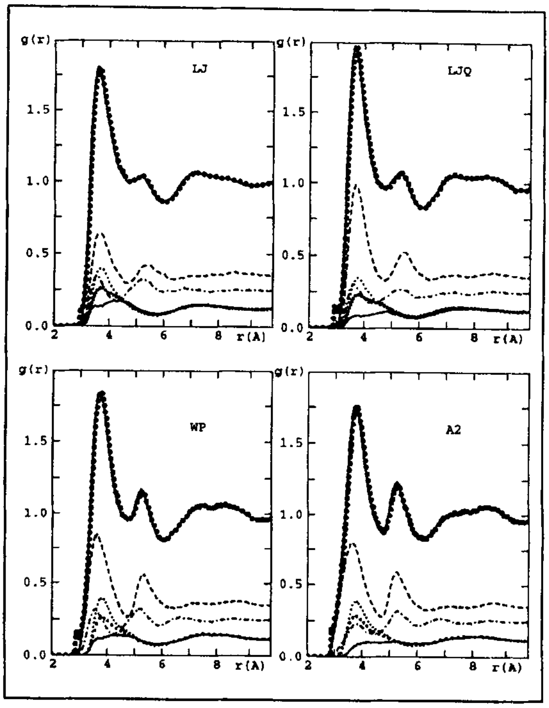

Figure 2 The total and partial atom-atom distribution functions $g_{aa}(r)$ obtained from MD and RMC data. The set of non-overlapping configurations Γ which fill all the angular space of a pair is reported in Table 1. From top to bottom the curves represent the total *g*(*r*) of MD(——) and RMC (●●●●), and the partial *g*(*r*) of T(- - - -), P(. . . .), LP (- · - · -), X(●●●●) and V(——).

potentials (A2 and WP) are able to better defining both the T and LP configurations giving in this way a better agreement with experiments. These behaviours are also evident in te centre-centre distribution functions of Figure 3. The partial contributions $g_{cc}^{\Gamma}(r)$ are defined as averages of the orientational pair distribution function, that is:

$$g_{cc}^{\Gamma}(r)=\frac{1}{\Omega}\iint_{\{\Gamma\}} g(r,\omega_1,\omega_2)\,d\omega_1\,d\omega_2 \tag{7}$$

where Ω is the total angular space of a pair and $\{\Gamma\}$ stands for the set of the limit angles of the configuration Γ. In that follows, the symbol Ω^{Γ} will be used to indicate the fraction of the angular space defined by $\{\Gamma\}$. By definition and from equation (7) it results $\Omega^{\Gamma}=\lim_{r\to\infty} g_{cc}^{\Gamma}(r)$. The five $g_{cc}^{\Gamma}(r)$ will be compared with those extracted from the particle configurations produced by the RMC procedure; if they are identical the angular space Ω^{Γ} can be reduced, the comparison repeated and so on until the leading geometries of Figure 1 are reached with an angular resolution (usually ± 10 °) compatible with the statistical noise.

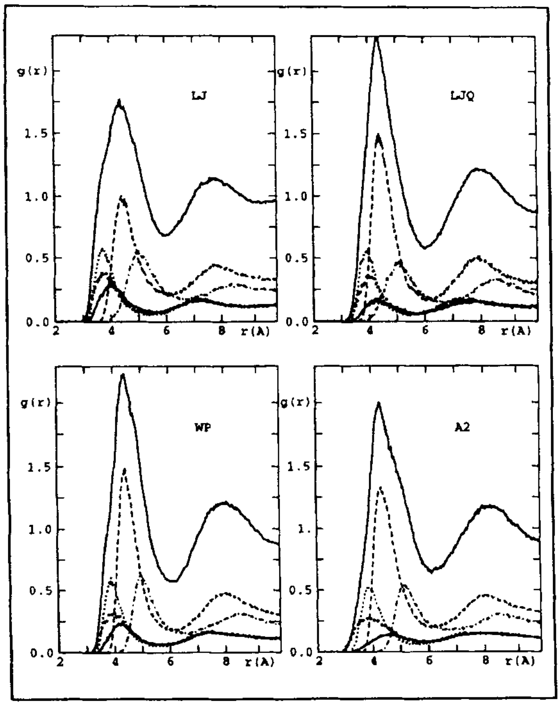

Figure 3 The total and partial centre-centre distribution functions $g_{cc}(r)$ obtained from MD data. The set of non-overlapping configurations Γ which fill all the angular space of a pair is reported in Table 1. From top to bottom the curves represent the total $g(r)$ of MD(——) and RMC (●●●●), and the partial $g(r)$ of T(- - - -), P(. . . .), LP(- · · · -), X(●●●●) and V(——).

3.2 *RMC simulation*

In all the simulations, the total $g_{aa}(r)$ of MD is used as input data of the RMC procedure. In Figure 2, the $g_{aa}(r)$ obtained by RMC and MD are compared. As is seen the overall agreement is generally good so that the particle configurations generated by RMC are consistent with the input 'experimental' data. Only at lowest r-values, around 3 Å where the $g_{aa}(r)$ starts to be different from zero, there is a small discrepancy which indicates that the total chi-square is not sensitive to the detail of the $g_{aa}(r)$ over a limited range of r. In other words, the repulsive part of the potentials is not 'simulated' by the particle configurations produced by RMC, which still show traces of the hard dumbbell interactions imposed by the constraints.

We can now perform the test a) by comparing the partial contributions $g^{\Gamma}_{cc}(r)$, predicted by the isotropic site-site LJ potential with their counterparts obtained from RMC simulation. In Figure 4, both the total (TOT) and partial distribution functions are shown. As is seen the total distribution function of RMC reproduces very well the MD one. The other five pictures, show the five configurations Γ computed from the particle configurations of MD and RMC via equation (7) for smaller and smaller solid angles Ω^{Γ}. The angular limits and the values of Ω^{Γ} are

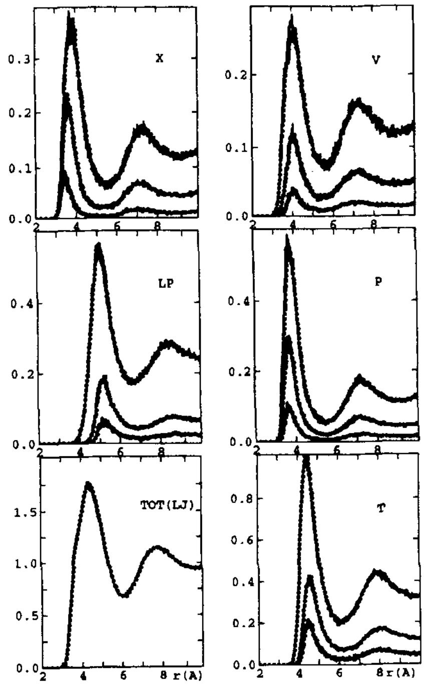

Figure 4 The total and partial centre-centre distribution functions $g_{cc}(r)$ for LJ potential by MD(——) and RMC (●●●●). For each one of the partial contributions $g^{\Gamma}_{cc}(r)$ the curves refer to the solid angles reported in Table 1. The lowerst curves of T and LP configurations have been multiplied by a factor of 3 for clarity.

reported in Table 1. The agreement is always very good up to the smallest solid angle Ω^{Γ} we have considered. Some samplings, performed for other solid angle values (not shown) return the same good agreement. Then we conclude that the particle configurations produced by RMC yield the same orientational correlation function $g(r, \omega_1, \omega_2)$ of MD. In these case the RMC technique is a valid tool for deriving the 'true' three dimensional structure by having in input only a one dimensional information represented by the atom-atom distribution functions $g_{aa}(r)$.

To perform the test b), the total and partial distribution functions obtained by MD and RMC are compared in Figures 5–7. As concerns the potential A2 (Fig. 5) the total $g_{cc}(r)$ agree fairly well. However, if one considers the partial configurations some discrepancies appear evident and are particularly strong for the V shaped configurations. For the other two potentials, LJQ of Figure 6 and WP of Figure 7, discrepancies between MD and RMC data are yet present on the total (TOT) $g_{cc}(r)$ and of course they are present on the partial $g^{\Gamma}_{cc}(r)$ too. Since the five $g^{\Gamma}_{cc}(r)$ are averages of $g(r, \omega_1, \omega_2)$ over each configuration Γ (see Eq. 7), we have to conclude that non central forces acting in these last three potentials disrupt the bijective correspondence between $g_{aa}(r)$ and $g(r, \omega_1, \omega_2)$. Consequently, the one to one correspondence between the potential $V(r, \omega_1, \omega_2)$ and the angular pair distribution function $g(r, \omega_1, \omega_2)$, which still survives, is not sufficient for determining the 'true' three dimensional structure. In other words, the use of the $g_{aa}(r)$ as input data and the addition of the hard dumbbell constraints are by themselves insufficient for guiding the RMC procedure towards the right three dimensional structure.

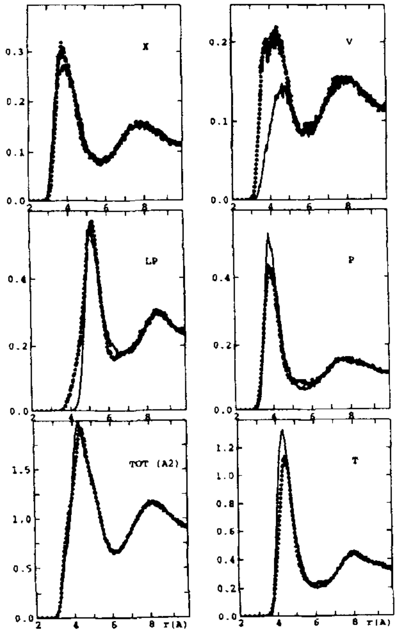

Figure 5 The total and partial centre-centre distribution functions $g_{cc}(r)$ for A2 potential by MD(——) and RMC (●●●●).

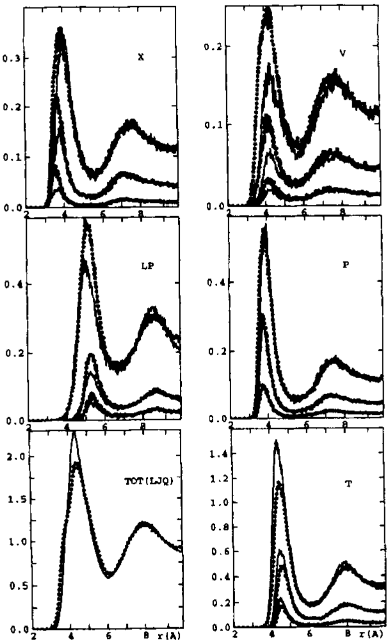

Figure 6 The total and partial centre-centre distribution functions $g_{cc}(r)$ for LJQ potential by MD(——) and RMC (●●●●). For each one of the partial contributions $g^{\Gamma}_{cc}(r)$ the curves refer to the solid angles reported in Table 1. The lowest curves of T and LP configurations have been multiplied by factors of 2 and 3, respectively.

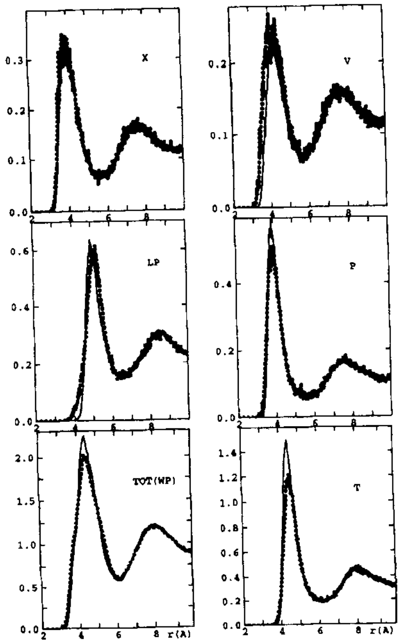

Figure 7 The total and partial centre-centre distribution functions $g_{cc}(r)$ for WP potential by MD(——) and RMC(●●●●).

Two final questions, concerning differences between the structure produced by MD and RMC, could be of interest, namely I) how much different the partial $g^{\Gamma}_{cc}(r)$ are when the solid angle Ω^{Γ} decreases, and II) how large differences RMC and MD structures produce in some observable physical properties. In Figure 6 (LJQ potential case), the partial $g^{\Gamma}_{cc}(r)$ are compared for the angular limits reported in Table 1. As is seen, no improvement is observed as Ω^{Γ} decreases; on the contrary the discrepancy tends to grow in general and becomes very large in the case of the cross connfigurations. It is worth remembering that $g^{\Gamma}_{cc}(r)$, computed over the smallest solid angle, corresponds to $g(r, \omega_1, \omega_2)$. From the literature [2], it is known that the first peak of $g(r, \omega_1, \omega_2)$ corresponds closely to the minimum of the potential energy $V(r, \omega_1, \omega_2)$ and that the deepness of the minimum determines the height of the peak. So, from Figure 6, it results that the RMC configurations underestimate the depth of the minimum of the T potential energy while overestimating that of X, V and LP. Then it is interesting to respond to the question II) by comparing the potential energies of the RMC and MD configurations. This can be done by using the interaction potential of MD to calculate the potential energy of the RMC configurations. The long range energy corrections have been neglected. The results are reported in Table 2. As is seen the predictions coincide in the case of LJ potential. For the anisotropic site-site potentials the RMC energies result always higher than the MD ones, the difference ranging from about 6% for A2 to about 17% in the case of WP. In case of liquid iodine, modelled by the modified A2 potential, the disagreement increases strongly, the RMC potential energy being twice that from MD [19]. This behaviour clearly shows that the RMC technique tends to produce the most disordered structure consistent with the data; the application of simple constraints, such as the rigid dumbbell conditions, are insufficient for determining the 'true' structure of the liquid. However, the quality of RMC lies in ability to include additional constraints, which means that additional order can be imposed. Thus, for example, one could impose, as a further constraint, to maximise the T configurations which are underestimated by all the anisotropic site-site potential; the physical meaning of this is that the electrostatic quadrupolar interactions, which favour the T shaped configurations, must be taken into account more than the other potential parts.

SUMMARY AND CONCLUSIONS

In this work we have studied the possibility of deriving reliable structural information on molecular diatomic liquids from the RMC simulation. The radial distribution

Table 2 Potential energy values obtained from particle configurations generated by MD and RMC. For both the potential function of MD has been used.

	LJ	*LJQ*	*A2*	*WP*
MD	$-1.81 \cdot 10^4$	$-2.01 \cdot 10^4$	$-1.61 \cdot 10^4$	$-2.07 \cdot 10^4$
RMC	$-1.81 \cdot 10^4$	$-1.80 \cdot 10^4$	$-1.52 \cdot 10^4$	$-1.73 \cdot 10^4$

function of atoms $g_{aa}(r)$ obtained from the conventional MD simulation has been used as experimental input for the RMC procedure. The potentials LJ, LJQ, A2 and WP have been considered for modelling liquid Chlorine near the triple point; all these potentials are pairwise additive so that the structure of the liquid is uniquely determined by the orientational pair distribution function, $g(r, \omega_1, \omega_2)$, since the irreducible three-body contributions are absent. However, while LJ is an isotropic site-site potential the three other contains different kinds of non central forces. Fitting the $g_{aa}(r)$ of MD, the RMC simulation has produced particle configurations whose $g_{aa}(r)$ agree with the input data for all the potential models. Then the three dimensional structures, due to MD and RMC, have been analysed in their orientational local order. A recently proposed general method, which relates the main features of the $g_{cc}(r)$ to the partial contributions of specific sets of pair geometries, the microscopic configuration Γ, has been applied; these contributions, $g_{cc}^{\Gamma}(r)$, represent the angular average of $g(r, \omega_1, \omega_2)$ within the limit angles of the configuration Γ and are therefore sensitive to the structural differences. It has been found that the $g_{cc}^{\Gamma}(r)$ of RMC and MD simulations agree very well in the case of the isotropic site-site LJ potential. This means that the one-to-one correspondence between site-site distribution function, $g_{aa}(r)$, the angular distribution function, $g(r, \omega_1, \omega_2)$ and the potential is very well reproduced by RMC. In this case, the RMC procedure is a valid tool for deriving the 'true' three dimensional structure and all the related physical properties of the system. In the case of anisotropic site potentials the $g_{cc}^{\Gamma}(r)$ of RMC and MD result significantly different and some observable physical properties, such as the potential energy, are different too. This leads us to conclude that from an experimental determination of the structure factor of diatomic liquids it is in general impossible to derive reliable structural information if only the constrain of hard dumbbells molecules is imposed. Indeed, while the approximation of additive potentials can be considered realistic, that of purely isotropic site-site interactions is certainly less reliable. The presence of quadrupolar and anisotropic site-site forces disrupts significantly the one-to-one correspondence between the potential and the site-site distribution function $g_{aa}(r)$. However, since the RMC is found to maximise the orientation configurational entropy, it is possible that the addition of further constrains could guide the RMC procedure towards the 'true' structure. For this purpose, the analysis in terms of configuration Γ can be particularly fruitful since it suggests what kind of dimer geometries (the T shaped one in case of liquid chlorine) are depopulated; their maximisation could be the further constraints the RMC simulation needs.

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