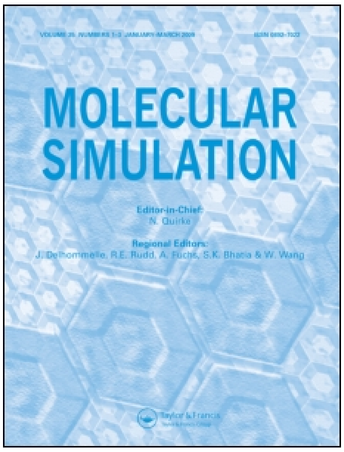

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

On the Bond-angle Distributions in Liquids and Liquid Solutions

M. Canales[a]; J. A. Padró[b]
[a] Department de Fisica i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Barcelona, Spain [b] Departament de Fisica Fonamental, Universitat de Barcelona, Barcelona, Spain

To cite this Article Canales, M. and Padró, J. A.(1992) 'On the Bond-angle Distributions in Liquids and Liquid Solutions', Molecular Simulation, 8: 6, 335 — 344
To link to this Article: DOI: 10.1080/08927029208022488
URL: http://dx.doi.org/10.1080/08927029208022488

Molecular Simulation, 1992, Vol. 8, pp. 335–344
Reprints available directly from the publisher
Photocopying permitted by license only

ON THE BOND-ANGLE DISTRIBUTIONS IN LIQUIDS AND LIQUID SOLUTIONS

M. CANALES

Department de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Pau Gargallo, 5. 08028 Barcelona, Spain

and

J.A. PADRÓ*

Departament de Fisica Fonamental, Universitat de Barcelona, Diagonal, 647, 08028 Barcelona, Spain

(Received October 1991, accepted October 1991)

Bond-angle distributions are used for the study of local orientational order in liquid systems. Bond-angles between a central particle and particles in both the first and second coordination shells are considered. Molecular dynamics calculations are carried out for determining the bond-angle distributions in a Lennard Jones liquid. The resulting distributions are compared with those obtained from stochastic simulations of a subset of atoms (solute) of the same system (solution). Although the radial distribution functions from the two simulations are in agreement, the bond-angle distributions show noticeable differences. Computer simulation findings are compared with results obtained by using both the superposition and convolution approximations. The reliability of the generalized Langevin dynamics simulation method is discussed.

KEY WORDS: Molecular dynamics simulation, generalized Langevin dynamics simulation, local orientational order, simple liquids, bond-angle distribution functions, solvent-averaged potentials

1 INTRODUCTION

Structural properties of liquids are normally described by the radial distribution functions ($g(r)$). These functions are directly related to the structure factors resulting from neutron diffraction experiments and are widely used in both theoretical and computer simulation studies. Although the pair $g(r)$ functions are the most significant, a complete description of the liquid structure would require to consider also other higher-order correlation functions ($g^n(\mathbf{r}_1, \ldots, \mathbf{r}_n)$) [1]. However, experimental information on high-order correlation functions is hardly available and reliable computer simulation (or theoretical) studies including these correlations would require to consider many body potentials which cannot easily be modeled. Hence, it is worth to know to which extent a close agreement between the $g(r)$ functions involves deeper structural similarities. This topic has been recently discussed [2, 3].

The local structure in disordered systems is frequently studied by means of the bond-angle distributions, i.e., the distribution of the angles subtended at a particular particle by pairs of neighboring particles. These distributions are intrinsically dependent

---

*To whom correspondence should be addressed.

on the triplet correlation functions ($g^3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$) [4] and they provide a suitable way for detailed examination of the differences between the structures of systems with the same $g(r)$. Bond-angle distributions in dense liquids of triplets made up of a central particle and two particles in the first coordination shell have been studied in several papers [3–6]. In this work, triplets with one or two particles in the second shell are also monitored.

One of the procedures which may be used for obtaining information on the structural details of liquid systems is the reverse Monte Carlo (RMC) simulation method [5, 7]. This method is based on the generation of a set of configurations which are consistent with a given $g(r)$ function (or structure factor). In a recent paper, Pusztai and Tóth [3] analysed the reliability of the extra structural information which may be gained through the RMC method. They compared the local structures (bond-angle distributions and rotational invariants of spherical harmonics) in configurations obtained from ordinary MC simulations with those from RMC. It was shown that the structure of the bulk liquids like argon or molten salts is largely determined by the $g(r)$ functions. Nevertheless, this conclusion cannot be applied to any system. One of the aims of this work is to extend the test to the case of liquid solutions by discussing the degree of uniqueness of the solute structures corresponding to a given solute–solute $g(r)$ function.

Liquid solutions are often studied at the McMillan–Mayer (MM) level of description [8]. Thus, the solvent particles are not explicitly considered and the intersolute forces are derived from solvent-averaged potentials which depend on the thermodynamic state of the system. The main structural features of dense liquids may be interpreted in terms of excluded-volume effects, since they are made up of closely-packed particles. On the contrary, when solutions are studied at MM level the exclude-volume effects are irrelevant because the mean distances between solute particles are normally greater than their diameters. Therefore, it can be expected that, at MM level, differences between structures with the same $g(r)$ can be larger than in the case of dense liquids.

In this paper, we examine the bond-angle distributions of solute particles in configurations resulting from two independent simulations which lead to the same $g(r)$ function. For the sake of simplicity, a simple Lennard Jones liquid is considered. It is assumed that a subset of particles of the system play the role of the solute whereas the remaining ones play the role of the solvent. Both molecular dynamics (MD) simulation of the complete system and generalized Langevin dynamics (GLD) [9] simulation of the solute particles are carried out. An effective solvent-averaged pair potential [10] ($W_{\mathrm{eff}}(r)$) which is able to reproduce the $g(r)$ resulting from MD is used in GLD simulation.

2 METHOD AND COMPUTATIONAL DETAILS

2.1 *Computer Simulations*

Liquid Kr at $T = 134.3\,\mathrm{K}$ and $\rho = 1.7956 \times 10^{-2}$ at Å^3 was simulated by MD. We considered 530 atoms of Kr in a cubic box with periodic boundary conditions. The Beeman algorithm, with a time-step of 10^{-2} ps, was used for the integration of the classical equations of motion. A Lennard Jones potential with the usual parameters for Kr was assumed for the interactions. Forces were truncated at 2.4σ.

A subset of 92 atoms (solute) of the same system were simulated by GLD. We

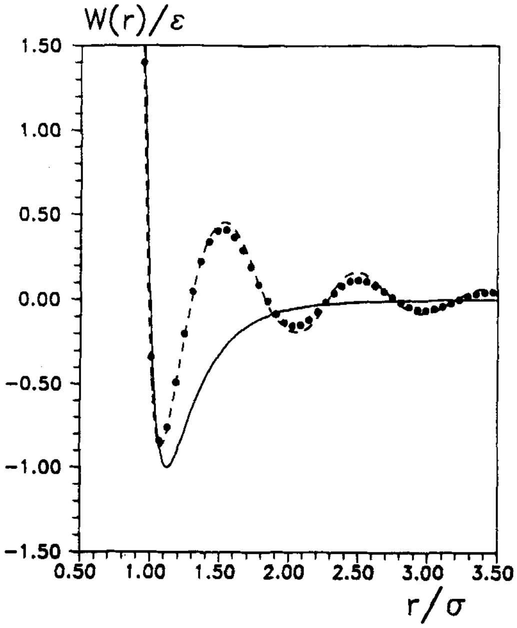

Figure 1 Interaction potentials. (——) Lennard Jones; (●●●) Effective solvent averaged potential ($W_{\text{eff}}(r)$) and (- - -) Mean force potential ($W_{\infty}(r)$).

considered the same box and periodic conditions as in MD. The temperature was also kept at 134.3 K. The generalized Langevin equations of motion were integrated according to the algorithm described in reference 9 using a time-step of 10^{-2} ps. It should be pointed out that the structural properties considered in this paper are independent of the model used for the friction and random forces. However, as in earlier papers [11, 12] we used an effective time-dependent memory function that yields to realistic motions of particles at short time scales.

The intersolute forces in GLD were calculated using the solvent-averaged $W_{\text{eff}}(r)$ potential shown in Figure 1. The $W_{\text{eff}}(r)$ potential was determined from the $g(r)$ resulting from the MD simulation by solving an effective Ornstein–Zernicke equation for the solute particles [10]. As may be observed in Figure 1, $W_{\text{eff}}(r)$ is very close to the mean force potential at infinite dilution ($W_{\infty}(r) = -k_BT \ln g(r)$). Interaction forces were truncated at 3.4σ, which correspond to the third $W_{\text{eff}}(r)$ maximum. Because of the slower decay of $W_{\text{eff}}(r)$, it was used a cutoff greater than in MD. As expected, the $g(r)$ function resulting from GLD using $W_{\text{eff}}(r)$ is in close agreement with the one from MD (Figure 2). In order to analyse the influence of the potential model, a complementary GLD simulation in identical conditions but using a Lennard Jones potential was also carried out.

2.2 Bond-angle Distributions

Bond-angle distributions are frequently used to represent the local angular correlations in disordered systems [3–7]. The angle (θ) between the vectors joining a central particle with two other atoms found within given distance intervals is called bond-angle. We

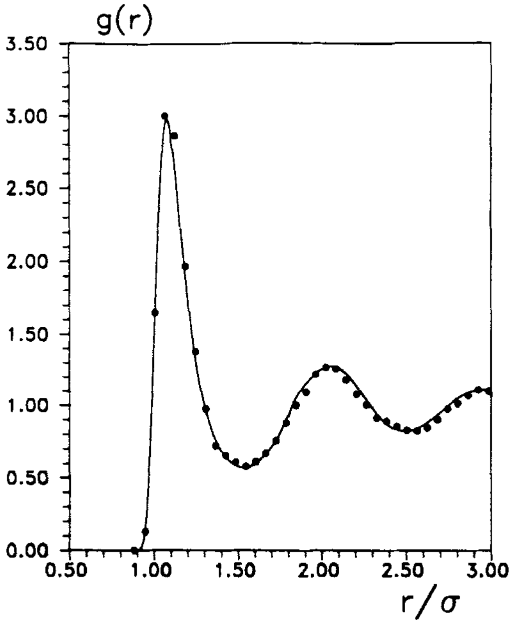

Figure 2 Radial distribution functions. (——) from MD; (● ● ●) from GLD with the W_{eff} (r) potential.

define the bond-angle distribution $P(\cos\theta, i)$ as the probability of occurrence of bond-angles with a cosine between $\cos\theta$ and $\cos\theta + d(\cos\theta)$. Parameter i characterize the distance intervals and probability is normalized for each i-value

$$\int_{-1}^{+1} P(\cos\theta, i) \quad d(\cos\theta) \;=\; 1 \tag{1}$$

For isotropic systems, the relation between $P(\cos\theta, i)$ and the triplet correlation function is [6].

$$P(\cos\theta, i) \;=\; A \int_{a_i}^{b_i} r^2 \mathrm{d}r \int_{c_i}^{d_i} r'^2 g^{(3)}(r, r', s)\mathrm{d}r' \tag{2}$$

where $s = (r^2 + r'^2 - 2rr'\cos\theta)^{1/2}$ and A is a normalization constant to be determined according to Equation (1). The limits of integrals correspond to the distance intervals for each i-value.

$P(\cos\theta, i)$ distributions for configurations obtained from MD and GLD simulations were calculated according to the procedure described elsewhere [6]. Distributions for $i = 1$ and $i = 2$ correspond to triplets with two particles in the first ($a_1 = c_1 = 0$, $b_1 = d_1 = 1.5\sigma$) or second ($a_2 = c_2 = 1.5\sigma$, $b_2 = d_2 = 2.5\sigma$) coordination shells, respectively (see Figure 2). Distributions for $i = 3$ correspond to triplets with a particle in the first coordination shell ($a_3 = 0$, $b_3 = 1.5\sigma$) whereas the other is in the second coordination shell ($c_3 = 1.5\sigma$, $d_3 = 2.5\sigma$). For the liquid considered in this work, the mean number of neighbours (calculated by integrating the $g(r)$) for the first and second shells were 12 and 43, respectively. $P(\cos\theta, i)$ results presented in the next Section were obtained by averaging over 10^8 particle triplets.

3 RESULTS AND DISCUSSION

3.1 MD Results

The bond-angle distributions obtained from the MD simulation are displayed in Figure 3. They show the characteristic trends of closely packed disordered structures. $P(\cos, \theta, i)$ for the first neighbours ($i = 1$) shows three peaks at $\theta = 55°$, 110° and 180°. The former corresponds to nearly equilater triangle configurations. The other correspond to configurations with one or two particles, respectively, between particles in the first coordination shell. These results are consistent with those found by Haymet [4] for a Lennard Jones liquid in similar conditions.

$P(\cos \theta, i)$ distributions for the second shell of neighbours ($i = 2$) show a sharp peak at 30° that corresponds to triplets with two close particles in the second shell. Peaks corresponding to triplets with one ($\theta = 60°$) or two ($\theta = 90°$) particles between atoms in the second shell are markedly smaller. For greater θ-values, $P(\cos \theta, i)$ does not show any significant maximum. Information on the relative positions of particles in the first and second shells is provided by $P(\cos \theta, i)$ for $i = 3$. In this case, the highest peak ($\theta = 35°$) corresponds to configurations with the particle in the second shell located at an intermediate position between the two particles in the first shell. This is consistent with the close packing of atoms in dense liquids. Triplets of atoms with collinear centers ($\theta = 0°$) are somewhat more probable than other with similar θ-values.

3.2 GLD Results

The bond angle distributions resulting from the GLD simulation reproduce the general trends of the MD findings (Figure 3). For small bond- angles, results from GLD and MD simultions are in good agreement, but clear differences may be observed for $\theta > 90°$ ($i = 1$). The disagreements should be associated with the non-additivity of the solvent-averaged potentials used in GLD. Non-additivity effects are more marked when other particles are located between the particles of the triplet (large θ-angles). For $i = 2$ and $i = 3$ the probabilities for large θ-angles are almost constant and comparison is not significant. $P(\cos \theta, i)$ distribution for $i = 3$ does not show the slightly higher probability for $\theta = 0$ shown by the MD results.

Despite the disagreements mentioned above, the relative distribution of particles in realistic systems (MD) is reasonably reproduced by GLD. Nevertheless, when $W_{\mathrm{eff}}(r)$ is replaced with a Lennard Jones potential, the $g(r)$'s from GLD and MD are in disagreement [13] and discrepancies between the solute structures are markedly larger (Figure 3). This suggests that solute structure cannot easily be reproduced by GLD simulations using bare potentials. It should be pointed out that rigorous deductions of the generalized Langevin equation for a system of interacting particles normally include interaction forces derived from bare potentials whereas the introduction of solvent averaged potentials appears less natural [14, 15]. However, solvent averaged potentials are commonly used, since GLD simulations with bare potentials which would be able to reproduce the main features of the solute structure would require very expensive simulations using tensorial memory functions dependent on the relative positions of particles. It should be noted that new integration algorithms and memory models would be developed for performing this kind of GLD simulations.

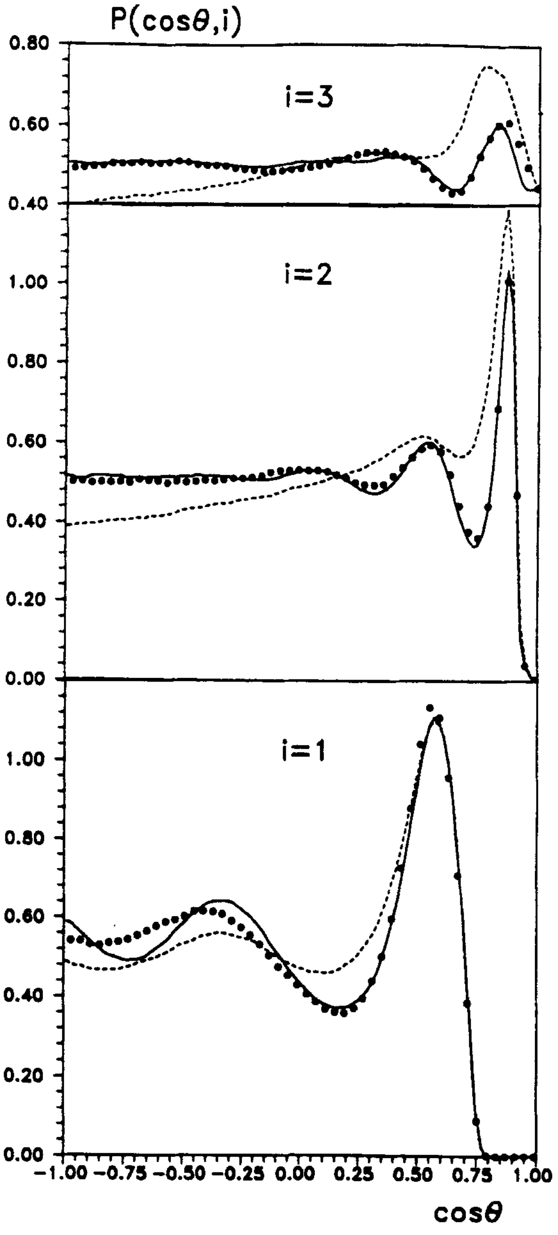

Figure 3 Bond-angle distribution functions. (——) from MD; (● ● ●) from GLD with the $W_{\mathrm{eff}}(r)$ potential; (- - - -) from GLD with the Lennard Jones potential.

3.3 Superposition Approximation

Theoretical calculations of the bond-angle distribution by Equation (2) require the knowledge of triplet correlation functions. These function are normally approximated by the Kirkwood superposition, i.e., by assuming that the triplet distribution may be expressed as a product of three pair distributions [1]. Then, equation (2) becomes [6]

$$P(\cos\theta, i) = A \int_{a_i}^{b_i} g(r) r^2 \mathrm{d}r \int_{c_i}^{d_i} g(s) g(r') r'^2 \mathrm{d}r' \qquad (3)$$

We have used this equation for calculating the P($\cos\theta$, i) distributions corresponding to our $g(r)$. As may be observed in Figure 4 the resulting distributions show noticeable disagreements with the MD findings for large θ-values ($i = 1$) but are very similar to the GLD results. This is consistent with the equivalence between the superposition approximation hypothesis and the pair-wise additivity assumption for the $W_\infty(r)$ potential[1] (it should be remembered that $W_\infty(r)$ and $W_{\mathrm{eff}}(r)$ are very similar, Figure 1).

3.4 Convolution Approximation

More refined approximations of the triplet distribution function have been proposed [1, 16]. $P(\cos\theta, i)$ distributions can be used for checking these approximations. In this work we have considered the convolution approximation [16]

$$\begin{aligned} g^{(3)}(r_{12}, r_{23}, r_{31}) = {} & 1 - g(r_{12}) - g(r_{31}) - g(r_{32}) + g(r_{12})g(r_{31}) + g(r_{23})g(r_{12}) \\ & + g(r_{31})g(r_{23}) + \rho \int h(r_{14})h(r_{24})h(r_{34})\mathrm{d}\mathbf{r}_4 \end{aligned}$$

where ρ is the density and $h(r) \equiv g(r) - 1$. The $P(\cos\theta, i)$ distributions resulting from this approximation (Figure 5) are in better agreement with the MD results than those from the GLD simulation or the superposition approximation. This shows that when the influence of other particles near to the particles of the triplet is taken into account (even at an elementary level) the $P(\cos\theta, i)$ distributions are improved. These findings corroborate that discrepancies between the MD and GLD results may be attributed to the non-additivity effects of the $W_{\mathrm{eff}}(r)$ potential.

4 CONCLUDING REMARKS

$P(\cos\theta, i)$ distribution provide a simple way for the description of structural details in liquids. Moreover, they can be very useful for testing theoretical approximations and models. Our results show that the solute structure in liquid solutions is not uniquely defined by the solute–solute $g(r)$ functions. This confirms that, in general, a close agreement of the pair distribution functions does not guarantee a complete agreement of other structural properties such as the triplet correlation functions.

When suitable solvent averaged potentials are used, GLD simulations yield to configurations that reproduce acceptably the main features of solute structures in liquid solutions. However, $P(\cos\theta, i)$ for large θ-angles show shortcomings due to the non-additivity of the solvent-averaged potentials. More accurate reproductions of the structural details would require to perform more expensive GLD simulations employing many body potentials or complex tensorial memory functions. In the case of RMC simulations, both the solute and solvent $g(r)$'s or higher order correlations would be

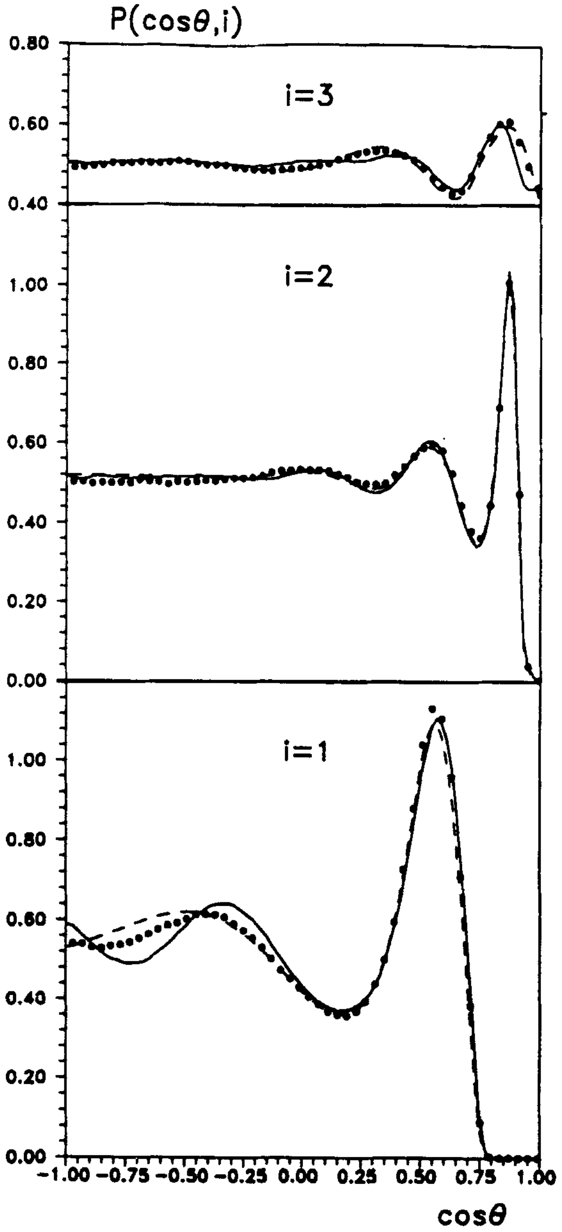

Figure 4 Bond-angle distribution functions. (——) from MD; (● ● ●) from GLD with the $W_{\text{eff}}(r)$ potential; (- - -) by using the superposition approximation.

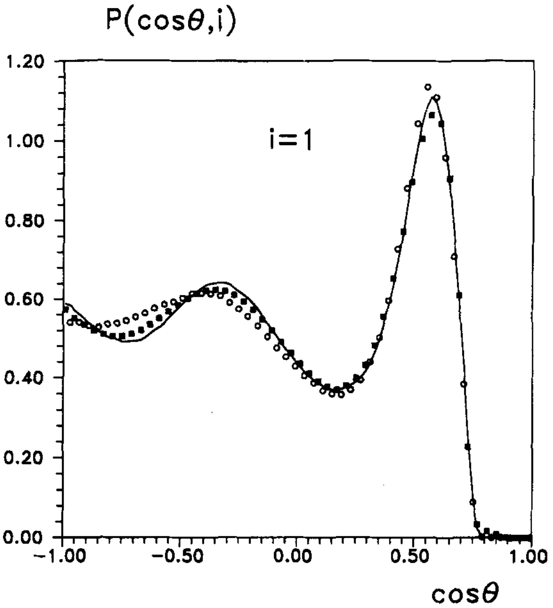

Figure 5 Bond-angle distribution functions. (——) from MD; (○ ○ ○) from GLD with the $W_{\text{eff}}(r)$ potential; (■ ■ ■) by using the convolution approximation.

imposed as input data. Nevertheless, the computational resources and microscopic information (potentials, memories, structure factors, etc.) required for performing such refined simulations are not available easily. Hence, approximate but realistic computer simulations, such as GLD employed in this work, will be very useful for the study of complex liquid systems.

Acknowledgments

We thank J. Boronat for his helpful suggestions and comments. The financial support of CICYT, Project PS 87-0026 is acknowledged.

References

[1] D.A. McQuarrie, *Statistical Mechanics*, **Chap. 13**, Harper and Row, New York (1973).
[2] R. Evans, "Comment on reverse Monte Carlo simulation", *Mol. Simul.*, **4**, 409 (1990).
[3] L. Pusztai and G. Tóth, "On the uniqueness of the reverse Monte Carlo simulation. I. Simple liquids, parcial radial distribution functions", *J. Chem. Phys.*, **94**, 3042 (1991).
[4] A.D.J. Haymet, "Orientational environments in liquids and solids", *Chem. Phys. Lett.*, **107**, 77 (1984).
[5] R.L. McGreevy and L. Pusztai, "The structure of molten salts", *Proc. R. Soc. Lond. A*, **430**,241 (1990).
[6] U. Balucani and R. Vallauri, "Evolution of bond-angle distribution from liquid to glassy states", *Chem. Phys. Lett.*, **166**, 77 (1990).
[7] R.L. McGreevy and L. Pusztai, "Reverse Monte Carlo simulation: A new technique for the determination of disordered structures", *Mol. Simul.*, **1**, 359 (1988).
[8] H.L. Friedman, *A Course in Statistical Mechanics*, **Chap. 4**, Prentice-Hall, New Jersey (1985).

[9] E. Guàrdia and J.A. Padró, "Generalized Langevin dynamics simulation of interacting particles", *J. Chem. Phys.*, **83,** 1917 (1985).

[10] E. Guàrdia, J.L. Gómez-Estévez and J.A. Padró, "Effective pair potentials at the McMillan-Mayer level", *J. Chem. Phys.*, **86,** 6438 (1987).

[11] G. Sesé, E. Guàrdia and J.A. Padró, "On the description of atomic motions in dense fluids by the generalized Langevin equation: statistical properties and random forces", *J. Stat. Phys.* **60,** 501 (1990).

[12] M. Canales and J.A. Padró, "Computer simulation study of relative diffusion in simple liquids", *J. Phys. Condens. Matter*, **3,** 7945 (1991).

[13] A. Giró, E. Guàrdia and J.A. Padró, "Langevin and molecular dynamics simulations of Lennard-Jones" liquids", *Mol. Phys.*, **55,** 1063 (1985).

[14] G. Ciccotti and J.P. Ryckaert, "On the derivation of the generalized Langevin equation for interacting Brownian particles", *J. Stat. Phys.*, **26,** 73 (1981).

[15] T.X. Xiang, F. Liu and D.M. Grant, "Generalized Langevin equations for molecular dynamics in solution", *J. Chem. Phys.*, **94,** 4471 (1991).

[16] E. Feenberg, *Theory of Quantum fluids*, **Chap. 2,** Academic, London (1969).