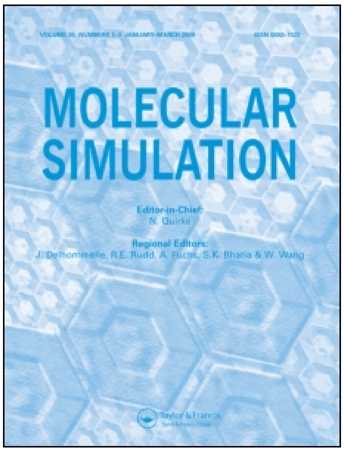

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REVERSE MONTE CARLO SIMULATION: A NEW TECHNIQUE FOR THE DETERMINATION OF DISORDERED STRUCTURES

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We have developed a new technique, based on the standard Monte Carlo simulation method with Markov chain sampling, in which a set of three dimensional particle configurations are generated that are consistent with the experimentally measured structure factor, A(Q), and radial distribution function, g(r), of a liquid or other disordered system. Consistency is determined by a standard χ^2 test using the experimental errors. No input potential is required, we present initial results for liquid argon. Since the technique can work directly from the structure factor it promises to be useful for modelling the structures of glasses or amorphous materials. It also has other advantages in multicomponent systems and as a tool for experimental data analysis.

KEY WORDS: Monte Carlo, structure factor, radial distribution function, liquid, glass.

INTRODUCTION

The conventional approach to an understanding of liquid structure can be summarised as follows:

Diffraction experiment
↓
Structure factor A(Q)
↓
Radial distribution function g(r)
↑
Molecular simulation
(Monte Carlo or molecular dynamics)
↑
Interatomic potential

Neutron or X-ray diffraction experiments give, after some small corrections, the structure factor A(Q). This may be Fourier transformed (provided that the Q range of the experiment is sufficiently large) to yield the radial distribution function g(r). Monte Carlo (MC) or molecular dynamics (MD) simulations based on an input interatomic potential produce sets of three dimensional particle configurations that may be averaged over to produce a one dimensional g(r). The experimental and simulation results may then be compared. If we wish to know about the details of local structural ordering, other than simply coordination numbers and average distances, we can in principle examine the three dimensional structure produced by the simulation, on the understanding that this is only valid if the simulated and experimental g(r) are in good agreement.

There are two disadvantages to this approach. Firstly we may not have a potential that adequately reproduces the experimental result. It is not generally possible to 'work out' the required potential simply from differences between the results. Secondly there is structural information that is easily apparent in A(Q), for instance peaks at low Q values, that is not apparent in g(r) since it involves small oscillations with a long r period. Comparison at the g(r) stage is not therefore ideal. The small size of the cell in most computer simulations limits the range of Q values for which A(Q) can be calculated directly, and hence comparison at this stage is not ideal either. To produce g(r) over a large enough r range that it can be transformed to A(Q) without serious truncation errors would require a simulation of $\simeq 5000$ particles, which is not generally practicable with realistic potentials, particularly if these have a long range component.

With the 'Reverse' Monte Carlo method described in this paper a three dimensional model of the structure can be produced that is sufficiently large to compare with experiment either as g(r) or as A(Q). The computer time required for this is of the order of hours on a typical mainframe, so the method may be widely applicable. The technique has a number of possibilities both for structural modelling and for experimental data analysis. No input potential is required; there may even be methods whereby the derived structures can actually be used to generate potentials.

REVERSE MONTE CARLO (RMC) SIMULATION

The Method

The algorithm for this method is essentially very simple, and easily understood by anybody familiar with standard MC techniques (see e.g. [1]). It may be summarised as follows:

1. We start with an initial configuration. This is a three dimensional array of N *points* in a cube of side L. The array may be generated at random, it may be a lattice, or it may be a set of coordinates generated in a conventional simulation.
2. Normal periodic boundary conditions are applied, i.e. the cube is surrounded by images of itself, and the radial distribution function $g_S(r)$, is calculated.
3. A new configuration is generated by random motion of one particle (point). The new radial distribution function, $g'_S(r)$ is then calculated.
4. These are compared with the experimental result for the system that is being modelled, $g_E(r)$, using a standard χ^2 test.

$$\chi^2 = \sum_{i=1}^{n_r} (g_E(r_i) - g_S(r_i))^2/\sigma_E^2(r_i) \qquad (1)$$

$$\chi'^2 = \sum_{i=1}^{n_r} (g_E(r_i) - g'_S(r_i))/\sigma_E^2(r_i) \qquad (2)$$

where n_r is the number of r points and σ_E is the experimental error.

5. If $\chi' < \chi$ the new configuration is accepted. If $\chi' > \chi$ it is accepted with a probability that follows a normal distribution, with width σ.
6. If the new configuration is accepted it becomes the starting configuration, otherwise the old configuration is retained. We then repeat from step 3.
7. The process is repeated until χ^2 decreases to an equilibrium value and oscillates about it, as with the energy in a conventional MC simulation. We then continue, saving one accepted configuration in N, again as in conventional MC. The average $g_S(r)$ calculated from these configurations agrees with experiment within experimental error, the errors having an approximately normal distribution.

This is the algorithim for comparison at $g(r)$ level. If we wish to compare A(Q) then the simulated $g_S(r)$ is transformed between steps 3 and 4,

$$A_S(Q) - 1 = \varrho \int 4\pi r^2 (g_S(r) - 1) \frac{\sin Qr}{Qr} dr \tag{3}$$

and in step 4, χ^2 is calculated using $A_E(Q)$ and $A_S(Q)$ rather than $g_E(r)$ and $g_S(r)$. Otherwise it is identical.

The original idea for using Monte Carlo simulation of an array of points to analyse liquid structure is due to Soper [2], who has applied it in one dimension to the complex case of water in porous media.

Note added in proof: since completing this manuscript the authors have discovered a number of earlier papers [16, 17, 18] in which the Reverse or Inverse Monte Carlo Method has been used to model a variety of physical data. The earliest of these is due to Kaplow et al. [18].

Calculation Details

When we begin the process it is necessary to calculate $g(r)$ in the normal way. However between each step it is only necessary to calculate the *change* in $g_S(r)$ due to the moved particle, rather than the complete $g'_S(r)$. Since the former takes a time approximately proportional to N, while the latter takes a time proportional to N^2, the saving is considerable for a large system. It is this that makes it possible to make N large, and hence to make L large enough that $g_S(r)$ can be transformed to $A_S(Q)$ without truncation errors.

$g_E(r)$ is zero below a certain value of r, r_0, corresponding to the fact that particles in the real system can only approach each other within a given closest distance. We can therefore automatically reject a new configuration at step 3 before calculating $g'_S(r)$ if the moved particle is within r_0 of any other particle. In a conventional MC simulation the maximum distance that a particle is moved between two configurations is chosen in order to make the ratio of accepted and rejected configurations some reasonable value, for instance 0.5. In this simulation this has not been found to be a reasonable approach, since it would result in a very small maximum distance, so the distance has been chosen to be a physically realistic value, 0.3 Å. The acceptance ratio is $\simeq$ 0.2 (see the following section).

When calculating χ^2 the values of $\sigma_E(Q)$ can be determined directly from experiment. They will be approximately constant except at low Q where they will tend to

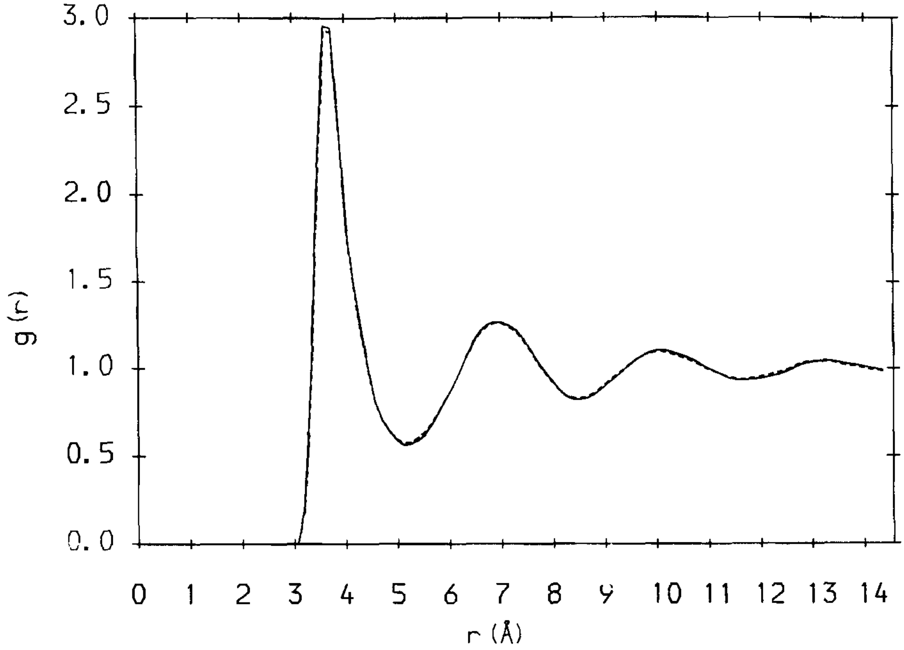

Figure 1 Radial distribution function g(r) for liquid argon; comparison of experiment [3] (solid line) and RMC calculation (broken line).

increase proportionately since $A(Q)$ is small. In the present case we have assumed $\sigma_E(Q)$ to be a constant, 0.03. However it is not obvious what to use for $\sigma_E(r)$ since $g_E(r)$ is the transform of $A_E(Q)$, and hence statistical errors will behave differently from systematic errors. In general $\sigma_E(r)$ will decrease rapidly with r, perhaps as $1/r^2$, but in this case we have also used $\sigma_E(r) = 0.03$. This difficulty with errors is another good reason for making comparison with experiment at the $A(Q)$ stage.

When comparison is being made at this stage, and a large simulation is therefore required, convergence from the starting point can be speeded up by the following method. We start with a small simulation (say 256 or 512 particles) and compare with $g_E(r)$ over the range $r = 0$ to $L/2$. When convergence has been achieved the size of the simulation is doubled to $2L$ and the new starting configuration created from 8 images of the final configuration with size L. If required this is repeated until the size is large enough to enable direct transformation to $A_S(Q)$. The criterion that a simulation is sufficiently large to enable transformation without truncation errors is that all oscillations in $r(g(r) - 1)$ have disappeared at $r = L/2$. At this point we then make a comparison of $r(g(r) - 1)$, since this is the quantity that is actually transformed to give $A(Q)$, before finally comparing to $A(Q)$.

Initial results

In Figure 1 we show $g_S(r)$ for liquid argon compared with the experimental result, $g_E(r)$ ($T = 85K$, $\varrho = 0.02125$ Å^{-3}), of Yarnell et al. [3] In Figure 2 $A_S(Q)$ is compared with $A_E(Q)$. The details of these simulations are given in Table 1.

Table 1 Simulation details and timings

	$g_S(r)$	$A_S(Q)$
N	512	4096
L (Å)	28.88	57.76
Starting configuration	Hard sphere simulation	Equilibrium config. from $g_S(r)$ ($\times 8$)
Number of moves to convergence (total/accepted)	10697/2070	68384/11420
Time to convergence (CPU mins)	6	425
Number of moves after convergence (total/accepted)	147391/25000	108751/16384
Time after convergence (CPU mins)	90	1115
Number of saved configurations	50	5
Time per saved configuration (CPU mins)	2	308
σ	0.06	0.06
σ_E	0.03	0.03
χ^2/n_r	0.075	0.05

The CPU time used (given for a VAX 8800) is comparable to that for a conventional Monte Carlo simulation, so the RMC method may be widely applicable. It is possible that the time may be reduced somewhat by refinements to the code, and since it is readily vectorisable the use of an array processor would result in a considerable increase in speed.

It can be seen in Figure 2 that $A_S(Q)$ only deviates significantly from $A_E(Q)$ for $Q < 1.5$ Å^{-1}, and that $A_S(0) = 0$. This is to be expected from the finite simulation size; since the number of particles within the box is fixed there can be no long wavelength density fluctuations, so the compressibility (which determines the $Q = 0$ value) is zero. In principle $A_S(Q)$ can be calculated down to $Q = 2\pi/L = 0.11$ Å^{-1}. Deviations may occur for Q larger than this because the total integral of $Q(A_S(Q) - 1)$ is fixed, so any deviations below $A_E(Q)$ at low Q must be matched by deviations above at higher Q.

DISCUSSION

We have so far given details of the algorithim and shown initial results for liquid argon. It appears that a three dimensional structure has been derived using one dimensional information, which is strictly impossible. However it is worth stressing at this stage that RMC is a method of *modelling* a structure, and only produces a result that is *consistent* with the experimental data. The three dimensional configurations

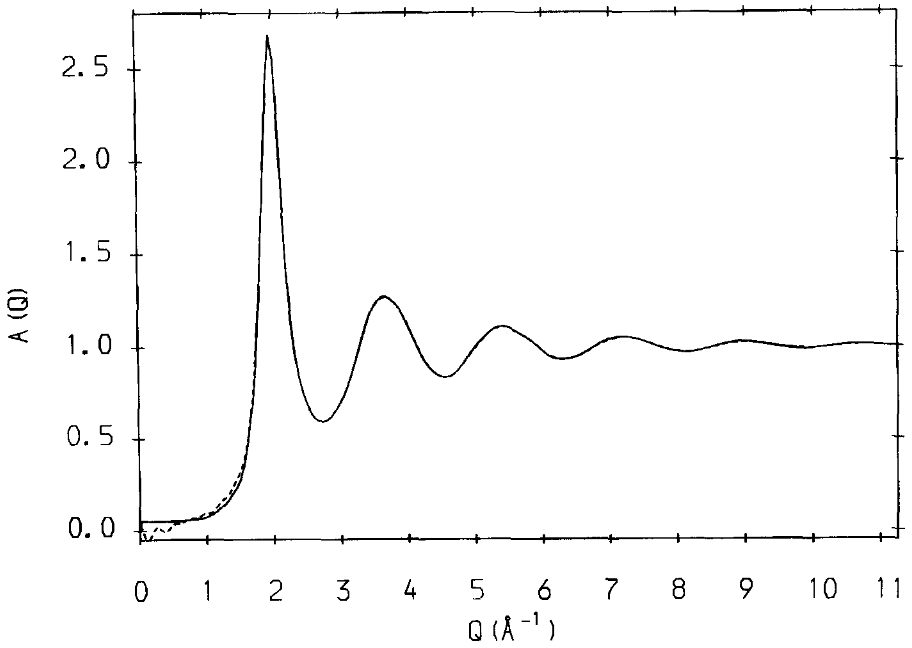

Figure 2 Structure factor A(Q) for liquid argon; comparison of experiment [3] (solid line) and RMC calculation (broken line).

produced are not unique, and those produced by other methods may differ in ways which may or may not be significant, depending on the application. In this respect they have as much validity as those produced by any other computer simulation. It is not possible to determine which technique produces the 'best' configurations, since comparison is necessarily based on a limited, and sometimes different, set of criteria. These may be radial distribution functions and structure factors or, for instance, thermodynamic and transport properties, depending on the method and aim of the simulation. The limitations should therefore be remembered, as with all simulations. It is also worth noting that RMC is no different in principle to the method of Rietveld refinement [4] that is widely used for determining crystal structures from powder diffraction patterns. Some possible applications of RMC are discussed below.

1. While experimentalists work hard to obtain accurate diffraction data for disordered systems the amount of information that is actually used, when the radial distribution function has been obtained, is generally very small. Normally this consists simply of the average atomic separation (first peak position) and the local coordination number (first peak integral). With the RMC method some more detailed ideas of real geometric structure can be obtained. The more accurately the structure factor is measured the more difficult it will become to obtain a three dimensional model that is consistent with it, and hence the more realistic that model becomes. Methods of determining and representing angular correlations, ranging from Voronoi polyhedra [5] to invariants of spherical harmonics [6] have already been developed to analyse the results of conventional simulations.
2. In experimental studies of the structures of glasses and amorphous solids there are

many techniques for obtaining structural models. While some results are obtained with conventional simulations these are often not in good enough agreement. Another approach is the creation of a physical 'ball and stick' model, relying on interpretation of the data and additional information such as known bond angles. The coordinates of such a model are then fed into a computer and g(r) calculated [7]. This structure may also be 'annealed' (Monte Carlo simulation at zero temperature) under a given potential, and then compared to experiment [8]. As with standard simulations this relies on an input potential. The size of the model is therefore limited and real comparison can only be made at the g(r) stage, which is unsatisfactory for the reasons already given. With the RMC method a three dimensional model can be created directly from the measured structure factor; additional information such as molecular bond angles can easily be included.

3. The neutron diffraction technique of isotopic substitution is now widely used to obtain the partial structure factors and partial radial distribution functions of disordered systems. For a binary system, for example NaCl [9], we can alter the scattering cross-section of Cl by using different mixtures of isotopes ^{35}Cl and ^{37}Cl. By making three measurements of the total structure factor $F(Q)$ for samples with different isotopic compositions we obtain

$$\begin{aligned} F(Q) &= b_+^2(A_{++}(Q)-1)+b_-^2(A_{--}(Q)-1)+2b_+b_-(A_{+-}(Q)-1) \\ F'(Q) &= b_+^2(A_{++}(Q)-1)+b'^2_-(A_{--}(Q)-1)+2b_+b'_-(A_{+-}(Q)-1) \qquad (4) \\ F''(Q) &= b_+^2(A_{++}(Q)-1)+b''^2_-(A_{--}(Q)-1)+2b_+b''_-(A_{+-}(Q)-1) \end{aligned}$$

   where + and − indicate the ions Na^+ and Cl^- respectively, and b_i is the scattering length of the relevant atomic species. We therefore have three simultaneous equations which can be solved to yield the partial structure factors $A_{ij}(Q)$. While this is in principle very simple it may in practice be very difficult due to the small differences between scattering lengths of the isotope, and the resulting poor conditioning of the system of equations. Complex iterative techniques of numerical analysis may have to be used [10].

   The RMC method can be used to compare a generated three dimensional structure, composed of more than one atomic species, with any number of total structure factors. If no suitable isotopes are available then only one structure factor is used, and additional information (such as discussed above for glasses) may need to be included in order to produce a 'realistic' structure. If isotopes are available then a number of total structure factors may be used; the partial structure factors and radial distribution functions obtained must necessarily therefore be consistent with a three dimensional structure, and hence with each other, which is not the case for conventional direct solution methods. Partial radial distribution functions, although one dimensional in themselves, contain information on three dimensional ordering when taken together, and this information is now used quantitatively rather than qualitatively.

When used as a technique for data analysis in this way, the RMC method may be readily extended to include effects such as experimental resolution. This may be particularly important for experiments using pulsed neutron sources [11], but will not be discussed further here. The maximum entropy (ME) technique [12] is at present gaining popularity as a method of data analysis that can similarly deal with problems such as errors and resolution. While RMC is not as fast as ME it has the advantage that considerable extra information, i.e. a three dimensional structure, is obtained.

4. One goal of theoreticians has always been to generate interatomic potentials using experimental diffraction data. This has been tried by inversion of the solution of one of the integral equation methods for calculating structure [13, 14]. The problem with this approach is that it relies on the validity of the particular integral equation, and the inversion is a complex iterative process. Now that a three dimensional structure consistent with diffraction data can be generated it is possible to think of new methods for generating potentials.

   One approach would be to use the Born–Green force equation [15]

$$-kT\nabla_1 g(r_{12}) = g(r_{12})\nabla_1\phi(r_{12}) + \varrho\int g^{(3)}(r_1, r_2, r_3)\nabla_1\phi(r_{13})dr_3$$

   where ∇_1 indicates differentiation with respect to r_1. Since the three particle correlation function $g^{(3)}$ can be calculated we can solve this integral equation to determine the force, $\nabla\phi$, and this can then be integrated to obtain the potential ϕ. The advantage of this method is that a numerical potential is obtained that does not have any pre-determined empirical form. The only assumption is that the potential is a pairwise additive function. Even if this is incorrect we would nevertheless obtain a 'mean field' two body approximation to the real many body potential.

These various applications will be discussed in more detail, and applied to real systems, in later papers.

CONCLUSIONS

We have described a new computer simulation method for the determination of disordered structures. The algorithim is simple, and has been shown to be sufficiently fast to be suitable for use on most mainframes. A number of possible applications have been discussed.

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References

[1] Hansen JP and McDonald IR. 'Theory of simple liquids'. Academic Press, London (1986).

[2] Soper AK, 'Structure of water in a confined geometry'. EPS conference on 'Liquids of small molecules'. Reggio, Calabria (1987).

[3] Yarnell JL, Katz MJ, Wenzel RG and Koenig SH, 'Structure factor and radial distribution function for liquid Argon at 85K'. *Phys. Rev.* A7 2130 (1973).

[4] Rietveld HM, 'The crystal structure factor of somed Alkaline Earth Uranates of the type M_3UO_6'. *Acta Cryst.* **20** 258 (1966); 'Line profiles of neutron powder-diffraction peaks for structure refinement'. *Acta Cryst.* **22** 151 (1967).

[5] Baranyai A and Ruff I, 'Statistical geometry of molten alkali halides'. *J. Chem. Phys.* **85** 365 (1986).

[6] Baranyai A, Geiger A, Gartrell-Mills PR, Heinzinger K, McGreevy RL, Palinkas G and Ruff I, 'Invariants of spherical harmonics as order parameters in liquids:. *Faraday Trans. II* **83** 1335 (1987).

[7] Wooten F and Weaire D, 'Modelling tetrahedrally bonded random networkds by computer'. *Solid State Physics* **40** 1 (1987).

[8] Ji-Chen Li and Cowlam N, 'Interatomic pair potentials for Metallic Alloy Glasses'. *Phys. Chem. Liq.* **17** 29 (1987).

[9] Edwards FG, Enderby JE, Howe RA and Page DI, 'The structure of molten sodium chloride'. *J. Phys. C* **8** 3483 (1975).

[10] Locke J, McGreevy RL, Messoloras S, Stewart RJ and Mitchell EWJ, 'The structure of molten CsCl'. *Phil. Mag. B* **51** 301 (1985).

[11] Howe MA, Howells WS and McGreevy RL, 'Measurement of the structure factor of molten CsCl using pulsed neutron source diffraction'. In preparation (1988).

[12] Johnson MW (ed.) 'Neutron Scattering Data Analysis' IOP conference series **81** (1986)

[13] Johnson MD, Hutchinson P and March NH, 'Ion-ion oscillatory potentials in liquid metals'. *Proc. Roy. Soc. London* **A282** 783 (1964).

[14] Levesque D, Weiss JJ and Reatto L, 'Pair interaction from structural data for dense classical liquids'. *Phys. Rev. Lett.* **54** 451 (1985).

[15] Born M and Green MS. 'A General Kinetic Theory of Liquids'. Cambridge University Press, Cambridge (1949).

[16] Dunn WL, Boffi VC and O'Foghludha F, 'Applications of the Inverse Monte Carlo Method in Photon Beam Physics'. *Nucl. Inst. and Meth.* **A255** 147 (1987).

[17] Gerold V and Kern J, 'The determination of atomic interaction energies in solid solutions from short range order coefficients – an inverse Monte Carlo method'. *Acta. Met.* **35** 393 (1987).

[18] Kaplow R, Rowe TA and Averbach BL, 'Atomic arrangement in vitreous selenium'. *Phys. Rev.* **168** 1068 (1968).