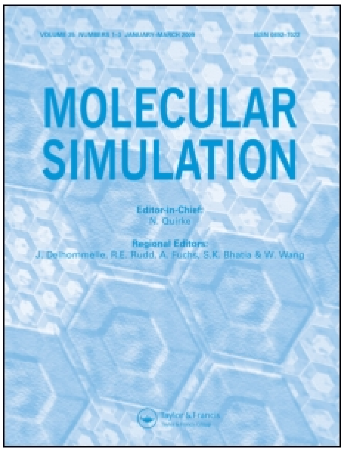
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

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

Test of the Inverse Monte Carlo Method for the Calculation of Interatomic Potential Energies in Atomic Liquids

M. Ostheimer[a]; H. Bertagnolli[a]
[a] Institut für Physikalische Chemie der Universität Würzburg Markusstr, Würzburg, FRG

To cite this Article Ostheimer, M. and Bertagnolli, H.(1989) 'Test of the Inverse Monte Carlo Method for the Calculation of Interatomic Potential Energies in Atomic Liquids', Molecular Simulation, 3: 4, 227 — 233

To link to this Article: DOI: 10.1080/08927028908031375

URL: http://dx.doi.org/10.1080/08927028908031375

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 1989, Vol. 3, pp. 227–233
Reprints available directly from the publisher
Photocopying permitted by license only

TEST OF THE INVERSE MONTE CARLO METHOD FOR THE CALCULATION OF INTERATOMIC POTENTIAL ENERGIES IN ATOMIC LIQUIDS

M. OSTHEIMER and H. BERTAGNOLLI

Institut für Physikalische Chemie der Universität Würzburg Markusstr. 9–11,
D-8700 Würzburg, FRG.

(*Received June, 1988; in revised form September, 1988*)

The principle purpose of this paper is to demonstrate the use of the Inverse Monte Carlo technique for calculating pair interaction energies in monoatomic liquids from a given equilibrium property. This method is based on the mathematical relation between transition probability and pair potential given by the fundamental equation of the "importance sampling" Monte Carlo method. In order to have well defined conditions for the test of the Inverse Monte Carlo method a Metropolis Monte Carlo simulation of a Lennard Jones liquid is carried out to give the equilibrium pair correlation function determined by the assumed potential. Because an equilibrium configuration is prerequisite for an Inverse Monte Carlo simulation a model system is generated reproducing the pair correlation function, which has been calculated by the Metropolis Monte Carlo simulation and therefore representing the system in thermal equilibrium. This configuration is used to simulate virtual atom displacements. The resulting changes in atom distribution for each single simulation step are inserted in a set of non-linear equations defining the transition probability for the virtual change of configuration. The solution of the set of equations for pair interaction energies yields the Lennard Jones potential by which the equilibrium configuration has been determined.

KEY WORDS: Monte Carlo simulation, Inverse Monte Carlo simulation, structure of liquids, interatomic potential

1. INTRODUCTION

In order to interpret the properties of liquids entirely by theoretical considerations it is necessary to relate an intermolecular potential to the microscopic structure. There are computer simulations as well as various theoretical approaches based on statistical mechanical theories [1]. The simulation methods of importance, Monte Carlo [2] and Molecular Dynamics [3], start from a given intermolecular potential and generate a sequence of particle configurations, from which the properties of liquids are deduced by averaging the corresponding molecular property over a set of configurations.

In this paper we will follow the inverse route. Starting from a given equilibrium configuration of an atomic liquid we will compute the interatomic interaction energies. This method, called Inverse Monte Carlo method (IMC), was introduced by Gerold and Kern [4] who used a computer generated model crystal of a binary solid solution of composition A_3B to simulate pair exchanges. For each virtual exchange the resulting change in the number of A-A pairs in various coordination spheres was calculated and registered. From these data the pair interaction energies were computed. However, due to the limited number of coordination shells and the fixed atoms positions the interaction potential energy could only be evaluated at four to eight interatomic distances. We have extended this method to atomic liquids and determined interaction potentials over the total range of interatomic distances of interest.

The advantage of the Inverse Monte Carlo method is evident, as it permits the computation of potentials directly from a given equilibrium configuration. This could be obtained even from an experimentally determined atom pair correlation function by fitting a model system. The current development shows, that the structure of molecular fluids can only be described by potentials taking into account the total variety of possible interactions. Due to the complexity of potentials the computational efforts to point out the essential terms and the related parameters are enormous by Molecular Dynamical and Monte Carlo methods. By inverse Monte Carlo simulation pair potential energies including all kinds of interactions (e.g. steric. electrostatic) determining the given structure can be calculated without any further theoretical assumptions.

2. THE INVERSE MONTE CARLO METHOD

The configuration of a given system of N particles is described by a set of position vectors $\{(\vec{r}_i)\}_k \equiv X_k$. According to "importance sampling" – Monte Carlo method [5] the transition probability p_k from one configuration X_k to another configuration X_{k+1} only depends on the change of energy

$$\Delta U_k = U_{k+1} - U_k \tag{1}$$

according to

$$p_k = \begin{cases} 1/\tau \exp\left[-\Delta U_k/k_B T\right] & \text{if } \Delta U > 0 \\ 1/\tau & \text{otherwise} \end{cases} \tag{2}$$

where τ is some arbitrary chosen factor, and usually is taken $\tau = 1$.

Assuming that the interaction between the particles can be approximated by discrete values $V(r_l)$ being constant within the distances r_l and r_{l+1}, the total change in energy ΔU_k caused by the k-th simulation step by varying the coordinates of an atom randomly by a maximum amount r_{max} is given by:

$$\Delta U_k = \sum_{l=l\min}^{l\max} V(r_l) \cdot \Delta n_k(r_l) \tag{3}$$

where $\Delta n_k(r_l)$ is the change of the number of distances in the interval $r_l \pm \Delta r$ in the model system. The total change of particle number $\Delta N(r_l)$ for one distance interval is obtained by summation over k_{max} individual changes multiplied by the transition probability p_k.

$$\Delta N(r_l) = \sum_{k=1}^{\mathrm{kmax}} p_k \cdot \Delta n_k(r_l) \quad \text{for } l = 1_{\min} \text{ to } l_{\max} \tag{4}$$

If the system is in the thermal equilibrium, the total change of neighbouring particles in each shell has to be constant for a sufficient large number k_{max} of simulation steps, i.e. the sum over all simulation steps has to be zero.

$$\Delta N(r_l) \approx 0 \quad \text{for } l = l_{\min} \text{ to } l_{\max} \tag{5}$$

The Inverse Monte Carlo method is based on validity of this equation. Starting from an equilibrium configuration a sequence of v_{max} virtual configurations is generated by successive random displacements of a periodically or randomly selected particle. The virtual changes $\Delta n_v(r_l)$ of the neighbouring atoms in each shell around the selected particle were determined. After a sufficient number of displacements the total sum of changes $\Delta N(r_l)$ according to equation (5) for each configuration shell is assumed to be zero.

The displacements must be virtually to keep the model system in thermal equilibrium. Satisfying the detailed balance conditions, c.f. equation (2), the transition probability is given by:

$$p_v = \exp[-\Delta U_v/k_B T] = \exp\left[-\left\{\sum_{l=l\mathrm{min}}^{l\mathrm{max}} V(r_l)\,\Delta n_v(r_l)\right\}/k_B T\right] \qquad (6)$$

Inserting expression (6) in equation (5) we obtain

$$\sum_{v=1}^{v\mathrm{max}} \Delta n_v(r_l)\cdot\exp\left[-\left\{\sum_{l=l\mathrm{min}}^{l\mathrm{max}} V(r_l)\,\Delta n_v(r_l)\right\}/k_B T\right] = 0 \qquad \text{for } l = l_{\mathrm{min}} \text{ to } l_{\mathrm{max}} (7)$$

The changes of the coordination number easily can be determined by virtual displacements. As equation (7) is fulfilled for each coordination shell, we obtain a system of equations, from which the values of interaction energy $V(r_l)$ can be calculated.

3. TEST OF THE INVERSE MONTE CARLO METHOD

3.1. Monte Carlo Simulation of Liquid Argon

In order to test the IMC method we have performed a Monte Carlo (MC) simulation of liquid Argon. Following the simulation of McDonald and Singer [6] we assume a Lennard Jones (12,6) interaction potential with the parameter values $\sigma = 3.405$ Å and $\varepsilon/k = 119.8\,K$ and a temperature of $T = 108\,K$. The system consists of 108 particles located in a cubic box of edge length 17.25 Å. This value corresponds to an average number density of 0.0211 Å^{-3}. Periodic boundary conditions are used. To speed up convergence rates the maximum values of displacements are chosen energy scaled [7]. The simulation is checked by comparing the energy and the atom pair correlation function with the results of Singer [6] and Wood [8], which have been reproduced.

3.2. Generation of an Equilibrium Configuration by the Construction of a Model System

The IMC method requires an equilibrium configuration to guarantee the correct application of equation (7). A MC simulation yields only equilibrium properties, but no single equilibrium configuration. Therefore a model system is constructed reproducing the equilibrium properties, which has been calculated by a MC simulation, and therefore representing the system in thermal equilibrium. As the microscopic structure of a liquid is characterized essentially by the atom pair correlation function, we used this function to generate the equilibrium configuration of the model system.

This technique has been used to interpret the structure and properties of amorphous solids [9–11] and it is based on the following principle. A macroscopic property of a model system containing N atoms, the positions of which characterize the configuration of the system, is calculated. The coordinates of a randomly or periodically selected particle are changed randomly, the resulting macroscopic property is computed and compared directly with the given quantity. If the displacement leads to a better agreement, the new position is accepted. This procedure is repeated until no further improvement can be achieved.

In our concrete case 1000 particles are located randomly in a sphere excluding shorter interatomic distances than 3.0 Å = 0.88 r/σ with a radius r determined from the required density. This choice of the number of particles is a compromise between a good statistic of distances and a tolerable computer time. Boundary problems are avoided by constructing a shell with thickness $r_{\max}$ around the sphere, where $r_{\max}$ is the maximum distance, up to that the interatomic separations are computed. Each particle of the inner sphere is taken as origin for calculation of the pair correlation function. The initial positions in the sphere are selected randomly and the corresponding atom pair correlation function is computed. Starting from this configuration a periodically selected particle is displaced randomly by 0.5 Å = 0.15 r/σ at maximum and the effect of this displacement on the atom pair correlation function is computed. If the position change improves the agreement with the atom pair correlation function of the MC simulation, the new position is accepted, otherwise rejected. This procedure is continued until the sum of least square errors, the criterion for acceptance, of the atom pair correlation function of the model system and of the MC simulation described in chapter 3.1 is less than 0.2%. As several simulations showed, the result is independent from the chosen starting configuration. As figure 1 shows, the computed atom pair correlation function does not exhibit any statistical noise despite of the fact, that no Gaussian broadening of individual distances or dampening function [11,12] is applied. This means, the number of atoms is sufficiently large to represent an equilibrium configuration exactly. The agreement between atom pair correlation functions is excellent.

3.3. The Inverse Monte Carlo Simulation

As already explained in chapter 2, the principle of this method is based on the determination of the resulting change of number of atom pairs within a discrete range of distances after a virtual displacement of an arbitrarily selected particle, which was chosen as origin of the corresponding pair distribution.

In principle following steps must be performed:

i) An atom is selected arbitrarily and its coordinates are changed virtually by an amount $\pm x_s \cdot S$, $\pm y_s \cdot S$, $\pm z_s \cdot S$, where S is the maximum displacement and x_s, y_s and z_s are independent random numbers between zero and one.

ii) For each distance interval r_l the net change of the number of atom pairs is calculated and stored separately.

iii) After a sufficient number of virtual displacements the determined changes $\Delta n_v(r_l)$ of the number of atom pairs are inserted in the system of equations (7), the solution of which gives the interaction potential in the distance range of consideration.

In detail following procedure is applied. For Argon the interval of distances was chosen between 2.5 Å and 8.0 Å corresponding to 0.73 r/σ and 2.3 r/σ with a stepsize of 0.1 Å. The value of the maximum displacement depends on the considered range in distance and the stepsize. Two restrictions exist. If the maximum displacement is

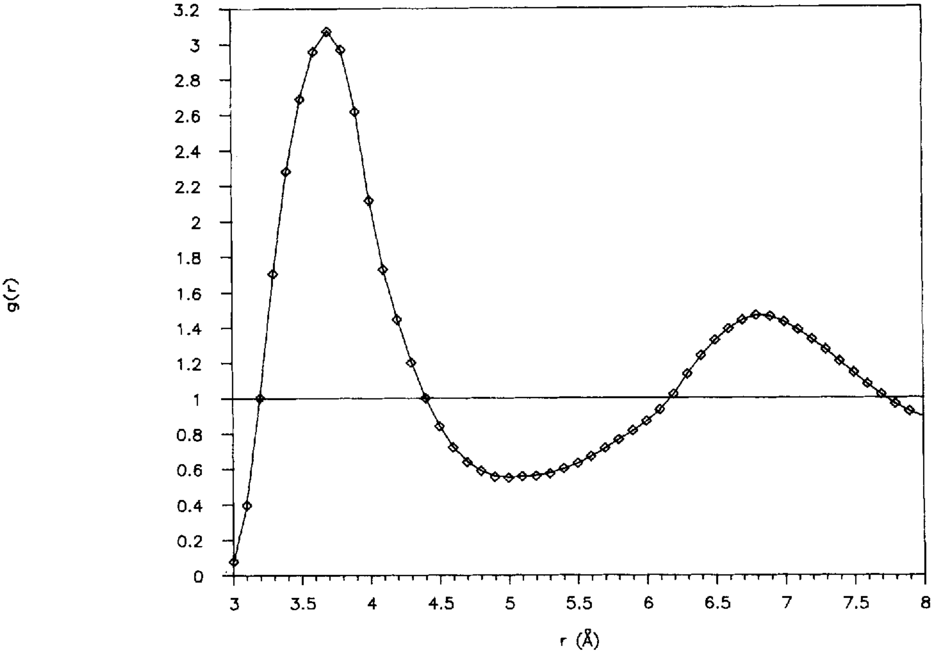


Figure 1 Atom pair correlation function obtained from a Monte Carlo simulation of liquid Argon at T = 108 K (solid line). This function was used to construct a configuration of a model system by ab initio Monte Carlo method. The pair correlation function of the model system is symbolized by ◇.

short (ca 0.5 Å $\approx$ 0.15 r/σ), the alteration of too many changes is within the stepsize and therefore only few changes are registered. If the maximum displacement is large (ca 2.0 Å $\approx$ 0.6 r/σ), too many changes are out of range of consideration. Therefore the best value is 0.3 - 0.5 r/σ (1 - 1.7 Å).

Equation 7 postulates that the sum over all changes of the number of atom pairs in each interval of atomic separation has to be zero. For this purpose a large number v_{max} of virtual displacements must be performed. To evaluate the minimum value for the number of simulation steps we performed several simulations. In the first test, where we have set v_{max} = 40.000, we have obtained an ill conditioned system of equations indicating the number of displacements being too small. The simulation run over 40.000 simulation steps yields not a smooth function for $V(r_i)$ and shows even a repulsive potential part for the distance interval [5.5 Å, 6.5 Å]. A number of at least 60.000 steps is sufficient to solve the system of equations without any irregularities. Under these conditions the solutions are independent of a further increase of v_{max} as a second simulation with v_{max} = 80.000 showed. The energy values are calculated by use of the IMSL-Subroutine ZSCNT, where a system of non-linear equations is solved iteratively [13]. The final solution is independent of the values that are chosen for $V(r_i)$ at the beginning of each iteration. The system of equations is solved by a separate program.

The resulting interaction energy values are represented in figure 2 together with the Lennard Jones potential used in the Monte Carlo simulation. The minimum of the calculated potential function exhibits a correct position and solely a deviation of ca

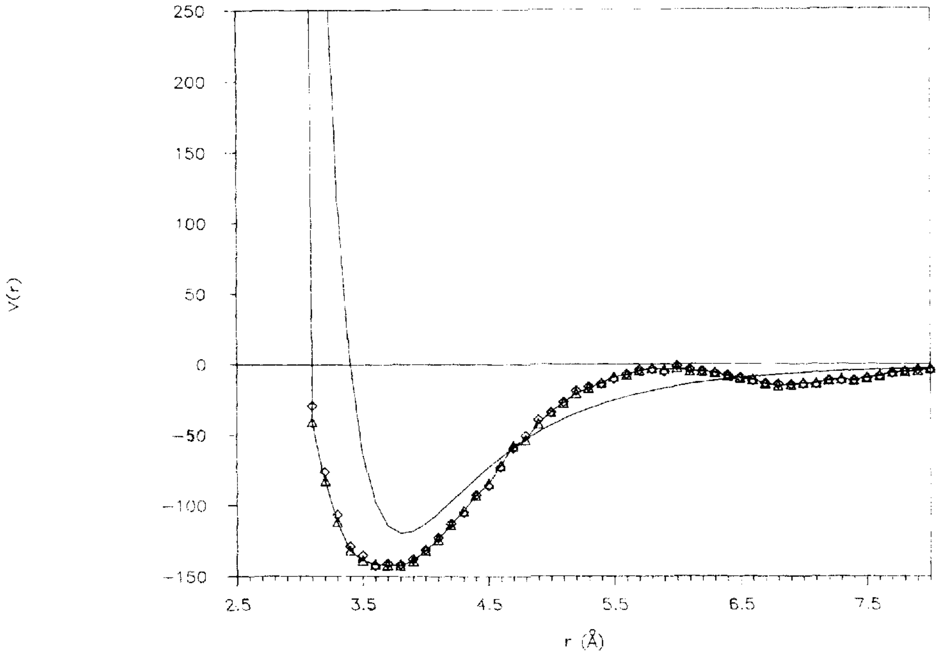


Figure 2 Comparison of the Lennard Jones potential used in the Monte Carlo simulation (solid line) with the corresponding functions determined by the Inverse Monte Carlo simulations. ◇ symbolizes the solutions of the system of equations after 60.000 virtual simulation steps and △△△ after 80.000 steps.

10% with respect to the Lennard Jones parameter ε. In the Monte Carlo simulation atomic distances less than 3.0 Å have been completely excluded. As a consequence of this restriction the repulsive part of the function can not be reproduced at small distances. Additionally the contribution of very short atomic separations is distributed over a range larger than the distance limit such leading to a broadening of the function. Furthermore the computed function shows spurious oscillations. The positions of the extrema coincide with these ones of the pair correlation function. May be the number of particles for the model system was too small or the function does not reflect only the single atom pair interaction, but also remaining contributions of many body interactions.

4. CONCLUSIONS

As our test demonstrates, the Inverse Monte Carlo method can be successfully applied to determine interaction potential energies of atomic liquids. However, an equilibrium configuration is required. For this test we have used an atom pair correlation function generated by a Monte Carlo simulation in order to fit the configuration of the model system. Of course this function can be replaced by experimentally determined atom pair correlation functions provided by X-ray or neutron diffraction experiments. The use of the Monte Carlo method for the generation of a model system in thermal equilibrium is not restricted to atomic liquid and can be easily extended to molecular liquids. In the case of molecular liquids the ambiguity, whether the actual configuration represents an equilibrium state or not, is drastically reduced by the possibility to use several independent diffraction experiments on identical liquid for the simultaneous fit of the configuration of the model system.

As the IMC simulation yields the interatomic interaction energies without any assumptions, the method permits the direct determination of the shape of potential functions, which would allow to fit analytical potential functions. This is very important for the study of such molecular liquids, for which the type and shape of interatomic interaction are unknown.

An additional advantage for the study of molecular liquids is that the interatomic potentials determined by use of IMC method implicitly contain the intermolecular geometry. Summarizing our results the IMC method offers interesting possibilities for a direct determination of interatomic potentials and therefore it can provide new information about the nature of interactions between molecules.

ACKNOWLEDGEMENTS

The authors thank Prof. Dr. V. Gerold and Dr. J. Kern for several helpful communications. The support of the Fonds der Chemischen Industrie is greatly appreciated.

References

[1] C.G. Gray and K.E. Gubbins, Theory of Molecular Fluids, International series of monographs on Chemistry Vol.9, Clarendon Press, Oxford, (1984).

[2] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth and A.H. Teller, "Equation of State Calculations by Fast Computing Machines", *J. Chem. Phys.*, **21,** 1087 (1953).

[3] B.J. Alder and T. Wainwright, Transport Processes in Statistical Mechanics, Academic, New York (1958).

[4] V. Gerold and J. Kern, "The determination of atomic interaction energies in solid solutions from short range order coefficients - an inverse Monte Carlo method", *Acta metall.*, **35,** 393–399 (1987).

[5] s.f.e. K. Binder, "Introduction: Theory and 'Technical' aspects of Monte Carlo Simulations", in Monte Carlo Methods in Statistical Physics, Topics in Current Physics, Vol.7, Springer Verlag (1979) and references cited here.

[6] I.R. McDonald and K. Singer, "Examination of the adequacy of the 12-6 potential for liquid Argon by means of Monte Carlo calculations", *J. Chem. Phys.*, **50,** 2308 (1969).

[7] S. Goldman, "A simple new way to help speed up Monte Carlo convergence rates: Energy-scaled displacement Monte Carlo", *J. Chem. Phys.*, **79,** 3938 (1983).

[8] W.W. Wood, "Monte Carlo studies in simple liquid models" in: Physics of Simple Liquids, North Holland, Amsterdam, (1968).

[9] D.E. Polk, "Structural model for amorphous Silicon and Germanium", *J. Non-Cryst. Sol.*, **5,** 365 (1971).

[10] M.D. Rechtin, A.L. Renninger and B.L. Averbach, "Monte Carlo models of amorphous materials", *J. Non-Cryst. Sol.*, **15,** 74 (1974).

[11] M.D. Rechtin, A.L. Renninger and B.L. Averbach, "Monte Carlo models of atomic arrangements in Arsenic glasses", *J. Non-Cryst. Sol.*, **16,** 1 (1974).

[12] G. Mason, "Radial distribution functions from small packings of spheres", *Nature*, **217,** 733 (1968).

[13] P. Wolfe, "The secant method for simultaneous non-linear equations", *Comm. of the ACM*, **2,** 12 (1959).