The Determination of the Microscopic Density in Liquids and Other Disordered Materials Using Reverse Monte Carlo Simulation

Orsolya Gereben[a]; LÁSzlÓ Pusztai[a]

[a] Laboratory of Theoretical Chemistry, L. Eötvös University, Hungary

PLEASE SCROLL DOWN FOR ARTICLE

THE DETERMINATION OF THE MICROSCOPIC DENSITY IN LIQUIDS AND OTHER DISORDERED MATERIALS USING REVERSE MONTE CARLO SIMULATION

ORSOLYA GEREBEN and LÁSZLÓ PUSZTAI

*Laboratory of Theoretical Chemistry, L. Eötvös University,
Budapest 112, POB 32, H-1518, Hungary*

A procdure using the Reverse Monte Carlo technique was shown to find the correct microscopic density of scattering centers (atoms, ions, etc.) in a model liquid within about 2%, on the sole basis of diffraction data. The method was also tested on solid amorphous systems of low, as well as of high packing fractions. An amorphous tetrahedral network served as a model for the former, while for the latter a model of a metallic glass was used.

KEYWORDS: Diffraction data, amorphous materials, backing fraction.

1. INTRODUCTION

The precise knowledge of the microscopic density of scattering centres – atoms, ions, atoms of molecules, etc. -, ϱ_0, in materials is of primary importance. The need for the correct values is especially expreessed in any kind of evaluation of diffraction data. Using the traditional data reduction, partial coordination numbers, which are the ultimate information in this case, are proportional to ϱ_0. On the other hand, it is impossible to build reliable structural models if wrong densities are applied.

There are many examples of liquid alloys where mixing of the components gives rise to a volume contraction (and, therefore, increasing density) that cannot be calculated correctly. Moreover, since these alloys are frequently highly corrosive, direct measurement of the density cannot be carried out easily.

The problem can also be extremely severe if the values of the average coordination number have extreme impact on the basic conclusions of a study. The best known example of such a case is that of the amorphous semiconductors, a-C, a-Si and a-Ge. Perhaps the most problematic is the case of thin films, where traditional methods are totally unfeasible.

Traditional (macroscopic) density measurements cannot usually be used for the determination of ϱ_0, since they simply give an m/V ratio of the whole sample (where m is the mass, V is the macroscopic volume of the sample). This ratio cannot count for voids that are much larger than the particles, and therefore the separation of particles may be predicted to be larger than the real distance between scattering

centres. (Also, a sometimes the volume of the sample is so small that the m/V ratio can only be measured with high uncertainities).

It is in principle possible to derive ϱ_0 from the initial slope of the so called reduced radial distribution function (rrdf), $G(r)$[1].

$$G(r) = \frac{2}{\pi} \int_{Q=0}^{\infty} Q(S(Q) - 1) \sin(Qr) dQ \qquad (1)$$

and

$$G(r) = 4\pi\varrho_0 r(g(r) - 1) \qquad (2)$$

where $S(Q)$ is the structure factor and $g(r)$ is the pair correlation function (pcf). Within the excluded volume region $G(r)$ should be a straight line with a slope of $-4\pi\varrho_0$. However, most of the errors of the direct Fourier transform accumulate in the same region. This problem makes the method no better than measuring m/V. This is why in earlier studies (see eg. Ref. 7) some rather *ad hoc* prediction of ϱ_0 were given, instead of using purely the above procedure.

It was noticed earlier[2] that it was not possible to fit experimental total pcf's by the Reverse Monte Carlo (RMC) technique[3] if wrong values for the density were used. This observation served as a starting point for the present study. It aims to explore the behaviour of the Reverse Monte Carlo technique if incorrect values of ϱ_0 are applied, using structure factors, as well as pcf's and rrdf's for dilute, and also, for dense model systems. On the basis of the experience to be gained from this survey we wish to propose that correct ϱ_0 values can be obtained by means of series of RMC simulations, in cases of good quality data. Note that to first order (for low absorption samples) in a neutron scattering experiment the structure factor is independent of density used for corrections (which is closely related to the macroscopic, m/V density of the sample).

2. REVERSE MONTE CARLO

The basic RMC algorithm has been described elsewhere in detail[3-5], therefore only the relevant parts are mentioned here.

RMC moves particles around randomly in the simulation box in order to reproduce a given set of diffraction data within the experimental uncertainities. In doing so, a quantity called χ^2 is calculated for each attempted move:

$$\chi^2 = \frac{\sum_{i=1}^{np} (X^C(y_i) - X^E(y_i))^2}{2\sigma^2} \qquad (3)$$

where X can be g, G or S and y can stand for r or Q. np is the number of data points, σ is related to the-assumed-experimental error. During the RMC calculation χ^2 decreases gradually until its value oscillates around an 'equilibrium' value. This

value is bound to a given σ value. Therefore it is important that if a comparison is made between two RMC fits (see below) then it can only be made properly if the value of σ was the same for both runs.

3. DESCRIPTION OF THE PROCEDURE LEADING TO ϱ_0

The number density is an input parameter of RMC. Changing the input ϱ_0 the equilibrium value of χ^2 (for a *given* σ) also changes. It was assumed that χ^2 has its minimum value if the correct ϱ_0 is put in.

In order to check this assumption series of RMC calculations were carried out for fixed sets of data, with different input ϱ_0 values. The initial ϱ_0^0 could usually be the latest value reported in the literature, and one lower and one higher value (by about 10 percents) were tried simultaneously. This meant at least 3 calculations per data set. From these three calculations it should be possible to establish a trend towards the correct microscopic density of scattering centres, provided that the above assumption is right.

In this work only model data sets corresponding to known ϱ_0's were applied. For establishing the correctness available by such a 'brute force' type method some calculation series applied a very fine ϱ_0 grid around the correct value. The reliability could then be estimated by comparing the correct ϱ_0 with the closest (to the correct) ϱ_0 value to which significantly larger χ^2 corresponded than to the correct (and known) number density.

4. CALCULATION DETAILS AND RESULTS

In order to assure the highest level of objectivity, the starting configuration and the length of the calculations were identical in each simulation for a particular data. For picking the right type of data, $g(r), G(r)$ and also $S(Q)$ have been modelled. Since it was assumed that the most direct data would be the most appropriate choice, the structure factor case was investigated for all the three of our model systems.

The first data set, representing a model simple liquid, was the best RMC fit to the structure factor of liquid gallium[6]. The number density of the model was 0.0525 Å^{-3}, corresponding to a packing fraction of about 0.33. The second data set was the best RMC fit to the structure factor of Etherington et al.,[7] for a-Ge. For the $g(r)$ case the corresponding pcf, given also by RMC, was applied. In order to test our approach under very different conditions we chose the best RMC fit to the three total coherent scattering functions, $F(Q)$, of $Ni_{62}Nb_{38}$ metallic glass[8] to be the third model data set. The corresponding partial pcf's provided by RMC served as input for the test calculations at $g(r)$ level. In this way, two rather different packing fraction values (0.344 and 0.841 (!), with ϱ_0 of 0.043 and 0.071 Å^{-3}, respectively) were tried out for the amorphous materials.

The models are discussed separately, and later on the application of different input functions ($g(r), G(r)$ and $S(Q)$) is compared. The main tool for presenting results will be graphs that show χ^2's as functions of the input ϱ_0. The reason for this

choice – apart from the desire for quantification – is that looking at RMC fits only does not reveal small differences in the quality of the fits.

A. The Case of Model Liquid Ga

The correct number density of the model was $0.0525 \, \text{Å}^{-3}$. In each calculation systems of $N = 1728$ particles were used, for modelling $g(r), G(r)$ and also $S(Q)$. The calculations last for $550000, 56000$ and 500000 accepted moves, respectively. Each simulation was started from an FCC lattice. The σ parameter was kept at 0.005 in each calculation.

Figure 1 gives χ^2-ϱ_0 curves for all the three series of RMC simulations. It is clear that, similarly to the amorphous models to be shown later, applying the structure factor provides an estimate of the correct number density within about 1–2%. Applying $g(r)$ leads to an incorrect estimate, although this model of a simple liquid behaves much better in this respect than more complicated structures.

It is also evident (though on the basis of a smaller calculation series, as modelling $G(r)$ went considerably slower than modelling $S(Q)$ or $g(r)$) that modelling the reduced radial distribution function, $G(r)$, also provides a sensible estimate on the correct ϱ_0, within about 2–4% (see Fig. 1). This clearly shows that the differences stemming from the application of different experimental information *cannot* be attributed simply to the different (r and Q) spaces where these functions are interpreted. Instead, the difference between data sets can be made upon the basis of that if they contain the number density explicitly, such as $S(Q)$ and $G(r)$, or do not, such as $g(r)$.

B. The Case of Model a-Ge

The use of $N = 1728$ particles with the model number density $\varrho_0 = 0.043 \, \text{Å}^{-3}$ resulted in a boxlength, L, of about $30 \, \text{Å}$. This system size proved sufficient for modelling
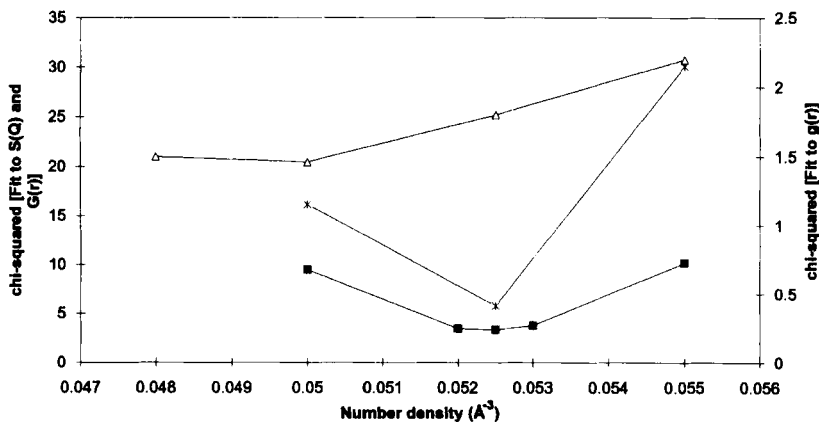

Figure 1   Minimum χ^2's as a function of the number density of scattering centres for the model of liquid Ga. The modelling was carried out in r space, using $g(r)$ (open triangles) and $G(r)$ (asterisks), as well as in Q space (full squares) using the structure factor. Note that here using $g(r)$ underestimates the correct density to a lesser extent than for the other models studied.

in r, as well as in Q space. The σ parameter in all the calculations was 0.005 (corresponding roughly to an assumed 0.5% of experimental uncertainity). In each calculation, 400000 accepted moves were completed, starting from the same initial configuration (which was a diamond lattice). In order to avoid unphysical configurations swiftly, a minimum value for the closest approach between particles, Δ, was applied. Throughout these computations Δ was kept constantly at $2\,\text{Å}$, which correlates to the experimental 'contact' value.

Figure 2 gives the χ^2-ϱ_0 curve for the model a-Ge system where the structure factor, $S(Q)$, was used as input for RMC. The minimum is found at the correct value of the number density of scattering centres, $\varrho_0 = 0.043\,\text{Å}^{-3}$, although the two closest densities worked with similar χ^2. This means that the uncertainty of the procedure in this case can be estimated to be about max. 2%. (Since the closest values of ϱ_0 applied were 0.042 and $0.044\,\text{Å}^{-3}$.) As it is evident from Figure 3, the RMC fits cannot easily be distinguished from each other, although the corresponding average coordination numbers are characteristically different (see Fig. 2).

The χ^2-ϱ_0 curve for the model a-Ge system where the pair correlation function, $g(r)$, was modelled is shown in Figure 4. Where the number density is higher than the correct value, the curve behaves like in the $S(Q)$ case, i.e. the fits are clearly poorer than the one where the correct ϱ_0 was used. However, when number densities that are *smaller* than the correct value are used, the quality of RMC fits even improves slightly, until ϱ_0 gets smaller than about $0.02\,\text{Å}^{-3}$. At first glance, this looks rather disappointing. But one should bear in mind that this kind of behaviour could be expected *a priori*- if the atoms have more freedom to move around then it is naturally easier to obey more complicated constraints. (This is why the results for the Q space modelling are noteworthy in themselves). The number density of
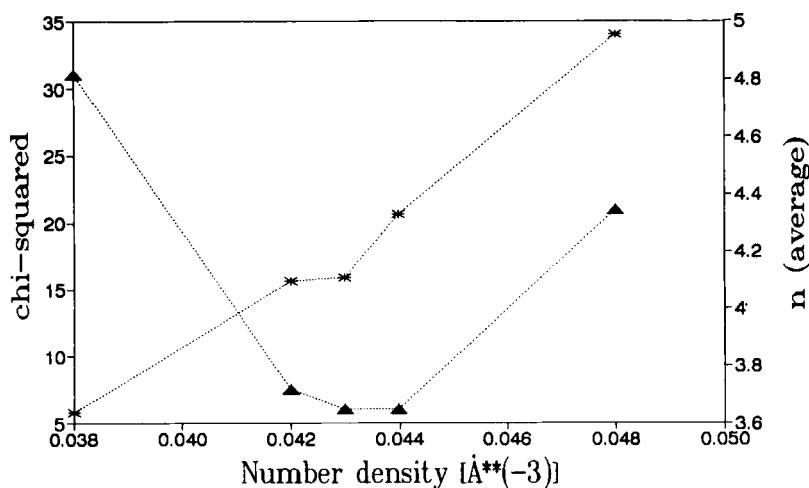

Figure 2 Minimum χ^2's as a function of the number density of scattering centres for the model of amorphous germanium. The modelling was carried out in Q space. Note the well defined minimum at the correct number density. The corresponding average first coordination numbers are also indicated. Filled triangles: χ^2; asterisks: $\bar{n}$.
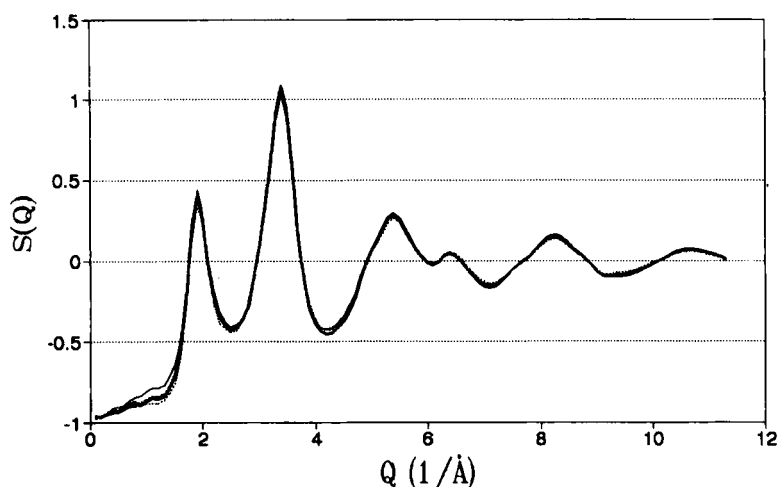
Figure 3 RMC fits to the structure factor of model a-Ge. Heavy solid line: original ($\varrho_0 = 0.043$ Å^{-3}); heavy dots: RMC fit with $\varrho_0 = 0.043$ Å^{-3}; solid: RMC fit with $\varrho_0 = 0.038$ Å^{-3}, dots: RMC fit with $\varrho_0 = 0.048$ Å^{-3}.

0.02 Å^{-3} means half of the correct packing fraction (using the same atomic size). Until this value the more freedom gained by the smaller number density could not be offset by the more complicated constraint imposed by the data with an incorrect ϱ_0. The apparent difference between using structure factors and pcf's should also be noted: the $S(Q)$ inherently contains the number density, whereas it is necessary to assume a value for ϱ_0 for obtaining $g(r)$. This might serve as an explanation why modelling in Q space provides different (better) evidence.
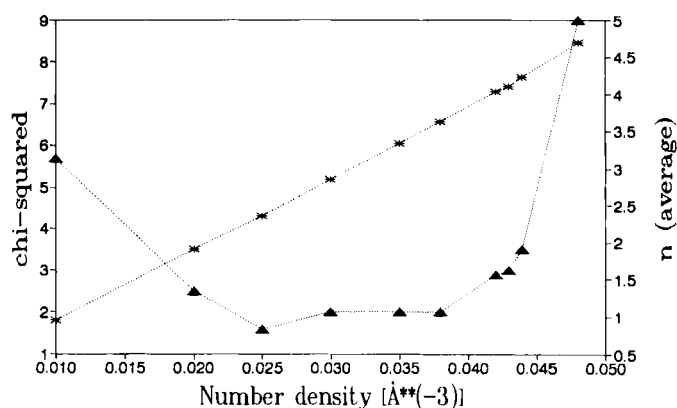

Figure 4 Minimum χ^2's as a function of the number density of scattering centres for the model of amorphous germanium. The modelling was carried out in r space. Note that densities higher than the correct value result in poorer agreement, but lower number densiy values can lead to slightly better fits. The corresponding average first coordination numbers are also indicated. Filled triangles: χ^2; asterisks: $\bar{n}$.

C. The Case of Model $Ni_{62}Nb_{38}$

Here the system sizes for modelling $g(r)$ and $F(Q)$ were different: for the former systems of 4096, whereas for the latter systems of 2596 particles were used. The σ parameter corresponded to an assumed 1% of experimental uncertainity, averaged over the three independent model $F(Q)$'s in Q space, and over the three model partial pcf's in r space. Minimum values of closest approaches between particles, Δ_{ij}, were applied during these series of calculations, as well. The values of $\Delta_{NiNi} = \Delta_{NiNb} = 2.2$ Å and $\Delta_{NbNb} = 2.4$ Å were kept constant throughout all the computations. The correct model number density, $\varrho_0 = 0.071$ Å^{-3} meant a packing fraction, $\eta = 0.841$, and this extremely high value caused difficulties in moving atoms around. For this reason a preliminary hard sphere Monte Carlo simulation of 1 million accepted moves, starting from a lattice with randomly distributed sites, was carried out for generating an appropriate initial configuration for the Q space modelling. Starting from this hard sphere configuration 500000 accepted moves were completed in each run, modelling the three $F(Q)$. For the r space calculations, where three model partial pcf's, $g_{ij}(r)$, were used as input, the final configuration of Ref. 8 served as initial configuration. (This explains the use of a larger system in r space.) In this series 60000 accepted moves were completed at each ϱ_0.

Figure 5 contains the $\chi^2 - \varrho_0$ curve for the case where $F(Q)$'s were modelled. (χ^2's are averages over the three data sets). Just as in the model a-Ge case, the true microscopic number density of scattering centres is estimated correctly within about 1% uncertainity.

Figure 5 contains a similar curve for the calculations in r space, as well. Again, the behaviour of the system resembles very much to what was observed in the case of model a-Ge. If higher densities were used than the correct value (0.071 Å^{-3}) then the quality of RMC fits deteriorated (χ^2's increased). On the other hand, if lower values for ϱ_0 were applied then in the interval of 0.071 Å$^{-3} \geqslant \varrho_0 \geqslant 0.065$ Å^{-3} the χ^2
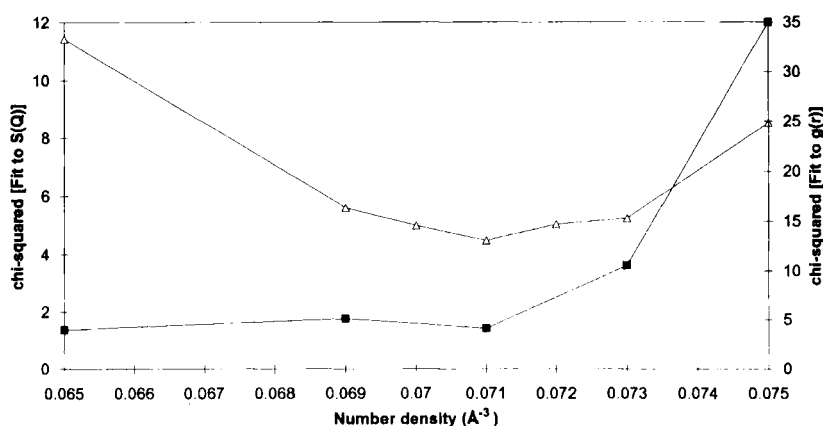

Figure 5 Minimum χ^2's as a function of the number density of scattering centres for the model of amorphous $Ni_{62}Nb_{38}$. The modelling was carried out in Q space (open triangles), as well as in r space (filled squares), using $g(r)$. Note the rather different behaviour of the two curves.

did not change significantly. This means that by means of modelling $g(r)$ it is not possible to estimate the correct number density unambigously. (Larger intervals have not been tested: probably somewhat lower densities would also work.)

5. DISCUSSION

It was demonstrated that if information ($S(Q)$, $F(Q)$ or $G(r)$), which *inherently* contains the microscopic number density, had been used for RMC modelling then the best fit (minimum value of χ^2) was obtained when the correct value of ϱ_0 had been applied. This statement is shown to be correct strictly for the case of atomic systems of low (model liquid Ga and amorphous Ge), as well as for high (model $Ni_{62}Nb_{38}$) packing fractions that have been investigated during this study. On the basis of the diversity of the models, however, it is suggested that Reverse Monte Carlo modelling is applicable for finding the appropriate number density of atomic disordered systems, provided that the proper structural information is applied. (For molecular systems further, more complicated investigations are needed.)

On the other hand, if $g(r)$ was used then RMC could fit the data equally well when lower number densities had been applied than the correct value of ϱ_0. Higher number densities, however, led immediately to worse agreement (considerably higher χ^2's). This can be interpreted as that $g(r)$ can impose only an upper limit for the number density, which is its correct value. The lower limit is more uncertain in this case.

Admittedly, the application of the procedure can be quite cumbersome, especially if no good estimate of ϱ_0 is present at the beginning. (Note that one can always get some estimate from $g(r)$ peak positions, so that the process described is to be used as a refinement.) For this reason, it cannot be expected that the determination of the microscopic density of scattering centres would be the easiest via this way in each case. It is thought that applying RMC for this purpose could be important particularly for thin films.

It is extremely important to notice that the procedure described above can work perfectly only if no other corrections are needed to be applied to the data than that of the density. (That is to say, 'perfect' experimental data is assumed, the only incorrect feature can be the number density). This, is however, a reasonable assumption for the data sets investigated in this work, as they had been corrected before for the usual experimental errors.

References

1. (*see eg.*) B. J. Thijsse, *J. Appl. Cryst.*, **17**, 61 (1984).
2. L. Pusztai, J. Sietsma and B. J. Thijsse, *Phil. Mag.*, **B**, in Press (1995).

3. R. L. McGreevy and L. Pusztai, *Molec. Sim.*, **1**, 359 (1988).
4. R. L. McGreevy and L. Pusztai, *Proc. Roy. Soc.*, *A*, **430**, 241 (1990).
5. R. L. McGreevy, M. A. Howe, D. A. Keen and K. Clausen, IOP Conference Series **107**, 165 (1990).
6. M.-C. Bellisent-Funnel, P. Chieux, D. Levesque and J. J. Weis, *Phys. Rev.*, *A*, **39**, 6310 (1989).
7. G. Etherington, A. C. Wright, J. T. Wenzel, J. C. Dore, J. H. Clarke and R. N. Sinclair, *J. Non-Cryst. Sol.*, **48**, 265 (1993).
8. L. Pusztai and E. Sváb, *J. Non-Cryst. Sol.*, **156–158**, 973 (1993).
9. O. Gereben and L. Pusztai, *Phys. Rev.*, *B*, **50**, 14136 (1994).