HOMOGENEOUS AND ISOTROPIC HARD SPHERE MODEL OF NON-CRYSTALLINE SOLIDS

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The Bernal-Mason-Finney algorithm for the numerical simulation of dense random packing of hard spheres as a model for the structure of amorphous solids is discussed. A very efficient and vast variant of this algorithm is described in detail. The constructed model was analysed and has been shown to be fairly homogeneous and isotropic in the sense that no angular dependence of the pair correlation functions is observed. The computer simulation using this method promises well to help understand metallic glass structures.

ОДНОРОДНАЯ И ИЗОТРОПНАЯ МОДЕЛЬ ТВЁРДЫХ ШАРОВ ДЛЯ НЕКРИСТАЛЛИЧЕСКИХ ТВЁРДЫХ ТЕЛ

В работе обсуждается алгорифм Бернала-Мэсона-Финнея для численного моделирования плотной случайной упаковки твёрдых шаров, которая служит моделью для структуры аморфных твёрдых тел. Детально описывается один очень эффективный и быстрый вариант этого алгорифма. Предложенная модель проанализирована и показано, что она фактически однородна и изотропна в том смысле, что не наблюдается угловой зависимости функций парных корреляций. Моделирование на счётно-вычислительной машине, использующее этот метод, даёт возможность в будущем понять также структуру металлических стёкол.

I. INTRODUCTION

Metallic glass alloys are an important new class of materials and research into them appears to be entering a stage of exponential growth. One of their most fundamental characteristics, their atomic structure, remains among the most elusive. A certain progress in understanding the arrangement of atoms in metallic glasses has been made by the development of methods of structural modelling. Models of non-crystalline aggregates can be built both in the laboratory and on a computer. The construction and study of physical assemblies is extremely laborious and the accuracy is limited. Computer simulations, especially computer-simulated dense random packing of hard spheres have shown good promise as zeroth-order representations of the atomic structure of metallic glasses and additional data processing procedures, such as energetic relaxation, give a good first order approach.

Most procedures which have been used to build hard-sphere models are sequential. Such is the method of Bennett [1], where each sphere is added successively to a previously existing tetrahedral site. The choice of a site can be varied, which leads with various boundary constraints to a lot of models similar in nature [2, 3, 4, 5, 6]. Once a sphere has been added, it is not moved further — a collective rearrangement is ruled out. The effective potential is a centrally acting gravity. Radial distribution functions are similar to the experimental ones. The density or packing fraction (ratio of volume occupied by spheres to the total volume) decreases with the distance from the centre of the cluster. It is believed that this nonphysical property results from the "softening" of pair correlations with the distance from the cluster centre [7]. Boudreaux and Gregor [7] have calculated pair correlation functions depending on some angular parameter. A strong anisotropy appears and it is proposed that the decrease in the density in the dense random packing structure is caused by the weakening pair correlations in the tangential directions. Clearly the packing occurs preferentially above and below any spherical shell and is insufficient to the sides. To obtain a correct model for studying, e.g., the alloy composition variation on pair correlation functions, or the effect of differences between the atomic sizes on amorphous solid formation, this anisotropic pair correlation and the decreasing density must be eliminated and one possible way is a modification of the simulation algorithm.

From this point of view another algorithm is promising. The algorithm used previously by Bernal [8] and Mason [9] on inadequate computers and recently more sucessfully applied by Finney [10], the so-called BMF algorithm, which simulates the compression of a hard sphere gas. In structural models built by using this method we do not expect density nonhomogeneities, while the only attractive force is the spherically symmetrical general compression and the collective rearrangements are allowed. The purpose of this paper is to discuss this method from the point of view of the calculation efficiency, homogeneity and isotropy of the constructed model.

II. THE SIMULATION ALGORITHM

The algorithm simulates the compression of the hard sphere gas under free boundary conditions. The Cartesian coordinates of N points are chosen within a large sphere by a pseudorandom number generator. Each such points is then considered to be the centre of a small sphere of diameter d. Alternatively a threedimensional simple cubic structure with a lattice parameter smaller than d can be built and the atom positions strongly randomized. Previous methods used a fairly simple straightforward scheme. If two spheres overlap, they are moved

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apart along the line of centres until they are just touching, irrespective of the overlaps that may be created thereby. The computer continues moving the spheres in a cycle until all overlaps have been removed (small cycle). Another (big) cycle is obtained after increasing the sphere diameter (or after rescaling the coordinates). Experience shows that the procedure produces clusters of increasing density. The cost of such a computer simulation is high. Most of the computing time is consumed in the checking on spheres overlap through the whole cluster. The procedure can be made more efficient in a similar way as that presented by Boudreaux and Gregor [7] in the case of the sequential building algorithm. Besides a list of coordinates of all spheres a three-dimensional integer map of the structure is held in the computer memory (or on the disk files). The map values are created simply by rounding-off the coordinates of spheres. Interspheres comparison need only be made between spheres in nearneighbouring boxes of the map. Every sphere is checked to see if it overlaps only with spheres from the 26 neighbouring boxes and after moving the overlapping spheres apart the map is partially updated. As a result of the integer character of the map the procedure is very fast.

When more than one sphere falls in a box of the map, only the first is taken into the calculations, the other follows in some of the next small cycles after updating the map. Also the more complicated four-dimensional maps were checked, but this simple one seems to be the most efficient from the point of view of the run-time of the computer. It is easily understood, as then the whole process is preferred in the area of the smallest density, it is on the periphery of the cluster.

III. ANALYSIS OF THE MODEL

The clusters built up using the BMF algorithm were analysed by Finney [10], here we restrict ourselves to the problems of homogeneity and the angular dependence of pair correlation functions only.

III.1. The packing fraction

As expected the clusters were spherical in shape and centred at the origin. The packing fraction was calculated for spherical samples with increasing radii cut from the packing. The actual volume of spheres within these radii was determined by calculating the volume of spheres totally within the radii and adding the inner sphere segments of those spheres intersecting the radii. The results for one cluster of 500 particles are shown in Fig. 1. The packing fraction is calculated after 1, 2, 5 and 9 big cycles. Except for small ripples near the origin the packing fraction is nearly constant over the cluster and at the edge begins to decrease rapidly.

To elucidate the angular variations of the packing of spheres four pair correlation functions have been calculated. Besides considering all the neighbours of every

sphere in turn, the inward pair correlation function has been constructed by considering only these neighbours which fall in a cone opening toward the centre of the model with an appex angle of 39°, the outward pair correlation function uses neighbours in an outwardpointing 39° cone and the tangential one is constructed using only those neighbours which are within 6° above or below a plane through the central atom and normal to a model radius.

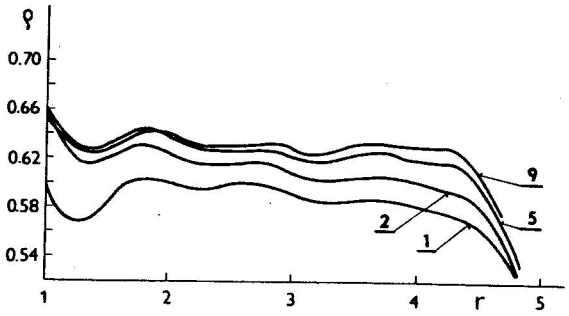

Fig. 1. The packing fraction ϱ of spherical samples of increasing radius cut from the cluster (after 1, 2, 5 and 9 big cycles).

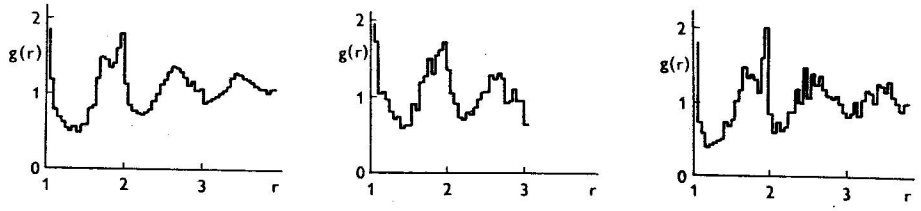

Fig. 2. Pair correlation functions of the model. Neighbours considered: a) in all directions — total pair correlation function; b) in tangential direction — tangential pair correlation function; c) in the direction of the cluster centre — inward pair correlation function.

All pair correlation functions have been calculated over all the 500 spheres in the cluster and corrections on the surface of the cluster similar to those used by Mason [12] have been applied. In Fig. 2 there are shown the total, tangential and inward pair correlation functions. The outward function is difficult to calculate correctly for such a small model, but its behaviour is similar at least for the first peak. One can see that the pair correlation functions are statistically similar, in contrast to results of Boudreaux and Gregor [7] who calculated the same functions for a model constructed by the Bennett sequential method and they observed a very strong weakening of the pair correlations especially in the tangential directions.

The second peak of pair correlation functions is split as it has been observed for most metallic amourphous solids and the amplitude of splitting increases with the packing fraction.

IV. CONCLUSION

Random arrangements of hard spheres originally proposed as models of the liquid state appear now to represent well also the state of amorphous metallic alloys, since in the regime of amorphous solid formation the interatomic packing is controlled in principle by two body repulsive forces. This paper has considered the Bernall-Mason-Finney algorithm for the numerical simulation of dense random packing of hard spheres. A very efficient and fast variant of this algorithm is described in detail. The constructed model was analysed and has been shown to be fairly homogeneous and isotropic in the sense that no angular dependence of the pair correlation function has been observed.

As the model has no structural nonhomogeneities and no angular anisotropy which may be very relevant to the real amorphous system, it is suitable for studying the atomic arrangement of metallic amorphous alloys. The model does not reproduce the position and relative intensities of the experimental pair correlation functions better than the others do and there is the problem of embedding the constructed cluster in a matrix of equivalent structure as a result of the used free boundary conditions. Nevertheless, because of its homogeneity, angular isotropy and because the method of simulation seems to represent better the real physical process occurring during the rapid cooling from the melt than the sequential building method, the computer simulation using this procedure may help to obtain an understanding of metallic glass structures, may help in our studies of alloy composition variations, stability regions of amorphous solids formations etc.

Work in progress at the time of this report includes an expansion of the model to include two or more sphere sizes and the effect of various atom pair affinities.

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