Influence of the packing effect on stability and transformation of nanoparticles embedded in random matrices

HELMUT HERMANN[*], ANTJE ELSNER, THOMAS GEMMING

Institute for Solid State and Materials Research, IFW Dresden, PF 260116, D-01171 Dresden, Germany

The compression of random hard sphere systems does not lead to the formation of iscosahedral short-range order. Instead, icosahedral clusters embedded in a hard sphere system with a medium packing fraction are not stable against densification and they dissolve with an increasing packing fraction. Random homogeneous hard sphere models with equal spheres transform into nanometre scale composites of face-centred cubic nanocrystals embedded in a dense random packed matrix when the mean packing fraction of 0.64 is exceeded

Key words: *hard spheres; nanostructure; liquid and amorphous metals; icosahedral order*

1. Introduction

There are experimental indications for the existence of clusters embedded in the matrix of the material in liquid and amorphous metallic alloys where the clusters and matrix differ with respect to their short-range order. Five-fold local symmetry [1] and icosahedral short-range order [2] have been recently detected in liquid metals. These experimental results re-activated the discussion about the classical icosahedron as a possible characteristic of the structure of simple liquids [3, 4]. Amorphous metallic alloys prepared from the liquid are often believed to retain some form of structural elements preformed in the melt. The formation of quasicrystalline particles observed in several metallic glasses could be a consequence of frozen-in icosahedral clusters. On the other hand, ultrafine crystalline particles of size about 1nm were detected in a series of amorphous metallic alloys [5–9]. The question of the existence or absence of clusters in liquids is relevant to the basic understanding of the structure of liquids.

_____

[*] Corresponding author, e-mail: h.hermann@ifw-dresden.de

With respect to amorphous metallic alloys it is known that nanometre scale precipitates may have considerable influence on the properties of the material.

The experimental observation of clusters or particles with diameters of the order of magnitude of 1nm is difficult and in most cases it is necessary to compare experimental data with model calculations in order to obtain reliable information. Important methods for this purpose are the simulation of high-resolution electron microscopy images [10] and the calculation of the scattering data [11].

There is a rich body of theoretical work on structure optimization and stability of isolated clusters. Frank [3] showed that a cluster consisting of 13 atoms interacting through a Lennard–Jones potential is most stable if there is a central atom surround by 12 neighbours situated on the vertices of an icosahedron. Detailed recent cluster calculations investigated the role of the interatomic potential and the dependence of structure and stability on the number and the type of atoms forming the cluster [12–14]. The problem of the formation of clusters with icosahedral order in extended systems of the order of 1000 atoms with periodic boundary conditions was studied [15–19] for different interaction potentials. While the simulations [15–19] led to local arrangements of atoms showing features of icosahedrality, the ab-initio calculations for liquid iron [20] resulted in structures characterized by pair distribution functions, which did not show the specific shape characteristic of icosahedral order. The ab-initio calculations are, of course, most accurate with respect to the interaction of atoms. They are, however, restricted to about one hundred atoms and are therefore not well suited to study the properties of clusters embedded in a liquid or amorphous matrix since a single cluster may already consist of about one hundred atoms.

The simplest approach to study systems of many particles is the hard sphere model. A review of the statistical theory of the packing of hard spheres is given in [21]. Both the quality of the algorithms and the range of applications of the hard sphere model have been developed continuously. Systematic investigations of binary mixtures of hard spheres [22] and continuous (truncated log-normal) distributions of radii [23], and the generalization of the so-called force-biased algorithm [24, 25] are important steps during this development. General problems of hard-sphere structures such as the question of whether or not random close packing of spheres is mathematically well-defined were also considered [26]. Investigations using packing algorithms are accompanied by molecular dynamics studies with hard spheres considering metastability and crystallization behaviour in hard-sphere glasses [27, 28].

In this paper, the model of hard spheres is used to study the behaviour of icosahedral and crystalline clusters in liquid and amorphous metals and metallic alloys. The repulsive interaction of two atoms is controlled by the hard core radii of the atoms which is the only parameter discriminating between different types of atoms. The attractive interaction is simulated by compressing the system of spheres using the described force-biased algorithm [25]. Periodic boundary conditions are applied to avoid surface effects.

2. Method

The first step in the simulation process is the preparation of an initial set of coordinates for the centres of the spheres. Two initial structures were considered: A random uncorrelated homogeneous distribution of coordinates (type 1) and icosahedral clusters embedded in a matrix of random uncorrelated coordinates (type 2). Each coordinate marks the centre of a sphere but the radii of the spheres may vary.

The second step is the densification of the system. The size of the systems analyzed ranged from 10 000 to 100 000. Systems with equal spheres and binary models are studied. In the latter case, the ratio of the diameters was 0.90 which corresponds to the ratio of the diameters of the central sphere to that of the outer spheres in an ideal icosahedral cluster.

The concept of a local packing fraction is used to characterize a given model. This structure parameter characterized the local environment of a sphere and is defined by the ratio of this sphere volume to the volume of its S-Voronoi cell. This cell was defined as follows: Select a sphere A and choose a random test point in the neighbourhood of sphere A. Calculate the distance d_A of the test point to the surface of sphere A and the distances of the test point to the surface of each other sphere situated in the neighbourhood A. If d_A is the smallest one of all distances then the test point belongs to the cell of sphere A. This procedure leads to a space-filling mosaic.

The neighbourhood of sphere A must be chosen in such a way that all spheres are included which may have an influence on the shape and volume of the mosaic cell of sphere A. The dimensions of the neighbourhood of a sphere and the number of test points determine the statistical accuracy of the calculated value for the local packing fraction. In these simulations, the statistical error was always below 0.3%. In a face-centred cubic crystal, the local packing fraction 0.74 is equal for all spheres. The central sphere of an ideal icosahedron is characterized by a local packing fraction of 0.76. The local packing fraction of a dense random packing model with equal spheres follows a monomodal distribution, and the global packing fraction (i.e. the total volume of the spheres divided by the volume of the box containing the spheres) is 0.64.

The distribution of the local packing fraction gives the basic information for discussing the structure of simulated hard sphere systems and the structural changes within them, especially for the identification of icosahedral and crystalline clusters in randomly packed matrices. Additionally, high-resolution transmission electron microscopy images can be simulated using the multi-slice method [10], and diffraction curves calculated by means of the well-known Scherrer formula.

3. Results

Figure 1 gives an impression of how a hard sphere model looks like. The model shown in Fig. 1was generated from a random initial distribution (type 1) of a binary mixture of hard spheres (size ratio 0.90 with a concentration of small spheres of 1/13).

The arrangement (global packing fraction: 0.65) is clearly non-crystalline but at several places the tendency to form local ordered clusters is visible. Fig. 2 shows the result of a simulation for a system of equal spheres (type 1). The global packing fraction of 0.66 is above the value for the classical dense random packing model (0.64) which points to partial crystallization.
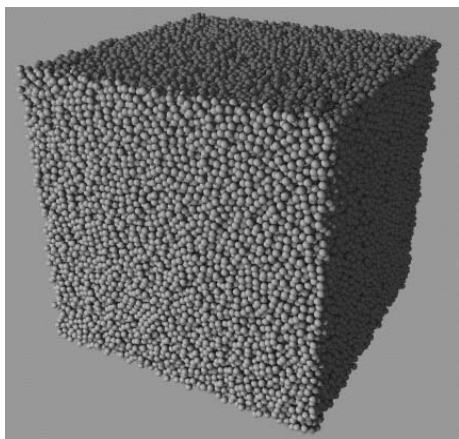

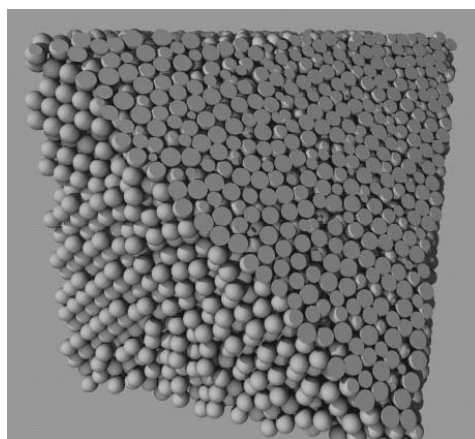Fig. 1. Hard sphere structure consisting of 100 000 spheres

Fig. 2. Cross-section of a partially crystallized system of 10 000 equal spheres

Nanocrystalline regions are visible at the (internal) surface of the model whereas the cross-section does not make the crystalline clusters visible. The model shown in Fig. 2 is a part of a systematic series of simulations. The following question was considered: Do clusters with a high local packing fraction appear when a dilute system of randomly arranged equal hard spheres is compressed? The answer is given in Fig. 3, showing typical frequency distributions of two highly compressed models: There is not one sphere with a local packing fraction of 0.76, i.e. icosahedral clusters are not created. Instead, a second maximum at 0.74 appears which points to the formation of face-centred cubic (fcc) or hexagonal crystallites.

Figure 4 shows the corresponding HREM images. The model with global packing fraction of 0.65 is still amorphous (or liquid) but for 0.66 the crystallites are visible and are shown to have cubic symmetry.

The diffraction patterns given in Fig. 5 are quite different, especially the splitting of the second peak. The maximum appeared at $2qR = 14.4$ which corresponds to the (220) reflection of fcc crystals and points to the transition from a homogeneous disordered state to a nanometre scale composite consisting of fcc crystallites embedded in an amorphous matrix.

In order to improve the conditions for the formation of icosahedral clusters binary models with size ratio of 0.90 (i.e., the diameter ratio of central and peripheral spheres in ideal icosahedra) were considered. The composition was also chosen as it occurs in a single icosahedron: 1 small central sphere and 12 large peripheral ones. Initial struc-

tures of types 1 and 2 were used. The type 2 structures are generated in the following way. Ternary hard sphere models are simulated with sphere radii of 0.90, 1, and 3. Then, the spheres with diameter 3 are replaced by icosahedral clusters each consisting of one central sphere of diameter 0.90 and 12 spheres of diameter 1. This procedure is illustrated in Fig. 6. The result is a binary system consisting of icosahedral clusters embedded in a binary system of hard spheres.
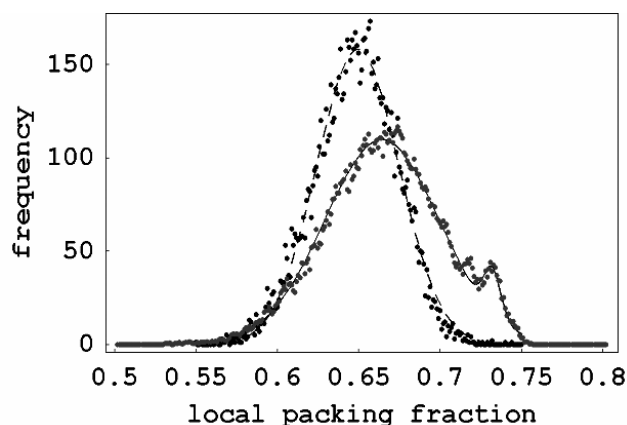

Fig. 3. Frequency distribution of local packing fraction and least-squares
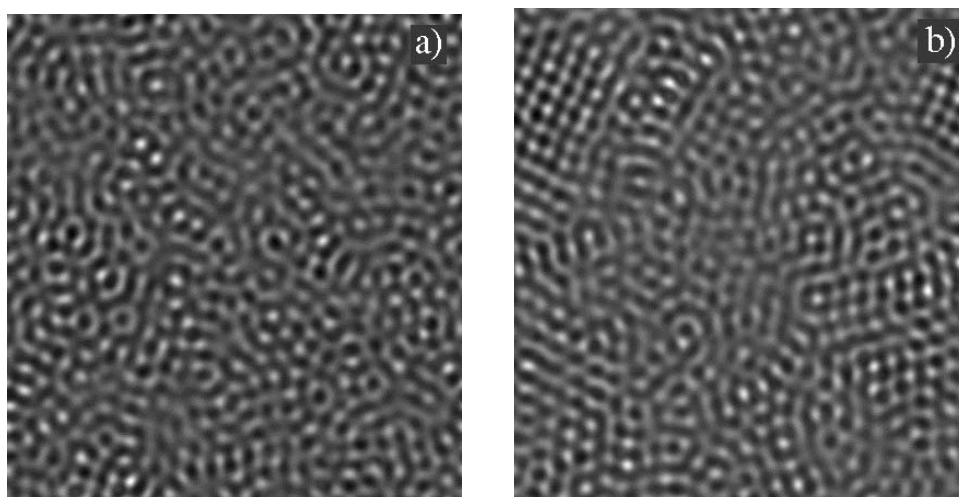fit by Gaussian functions; mean packing fraction 0.65 (dashed line) and 0.66 (solid line)

Fig. 4. HREM images of models with mean packing fraction of 0.65 (a) and 0.66 (b)
simulated for a Tecnai F30 microscope operated at 300 kV

Both systems were subjected to the compression routine, and for a sequence of global packing fractions the S-Voronoi analysis was carried out. Figure 7 shows the distribution of local packing fraction for the small spheres for representative steps.
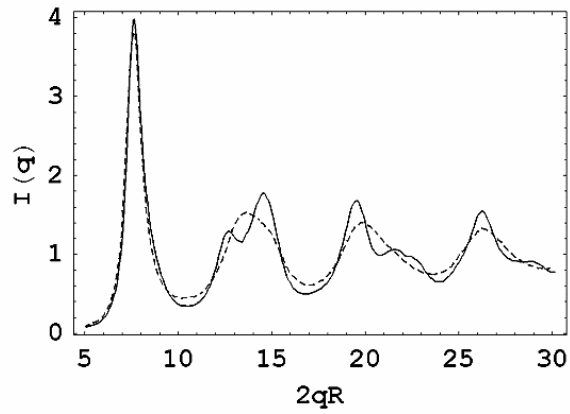
Fig. 5. Diffraction patterns of the model
with mean packing fraction
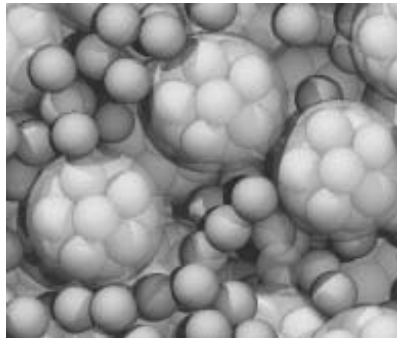0.65 (dashed line) and 0.66 (solid line)

Fig. 6. Preparation of initial structures
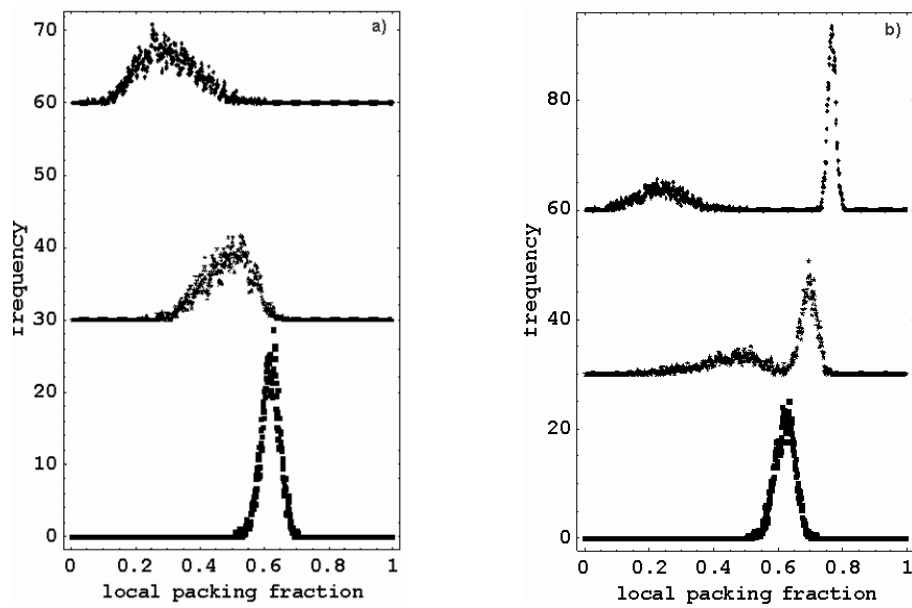including icosahedral clusters

Fig. 7. Frequency distribution of local packing fraction of small spheres
for random initial structure (a) and with icosahedra embedded in the initial state (b). Initial state,
mean packing fraction 0.30 (top), mean packing fraction of 0.50 (middle) and 0.64 (bottom)

The distribution for the initial type 1 structure is monomodal and centred at the mean value of 0.3. The width decreases during densification and the maximum is shifted to higher values. The distribution is zero above 0.70 which means that no icosahedral clusters appear in the non-crystalline state. The distribution of the system containing icosahedral clusters in the initial state shows different behaviour. The icosahedra are clearly detected by the sharp maximum at 0.76 whereas the small spheres distributed in the random matrix give rise to the broad maximum situated at a low local packing fraction. During densification, the broad maximum characterizing the small spheres in the random matrix is shifted to a higher local packing fraction, but the icosahedral peak moves towards lower values. Both distributions overlap and form a common distribution in the final state. No residue of the initial icosahedral order can be detected and no significant difference of the distributions of local packing fraction for type 1 and type 2 structures can be observed in the final state.

The diffraction patterns (Fig. 8) show the same tendency. The random and the icosahedral initial state can be distinguished by the diffraction curves.
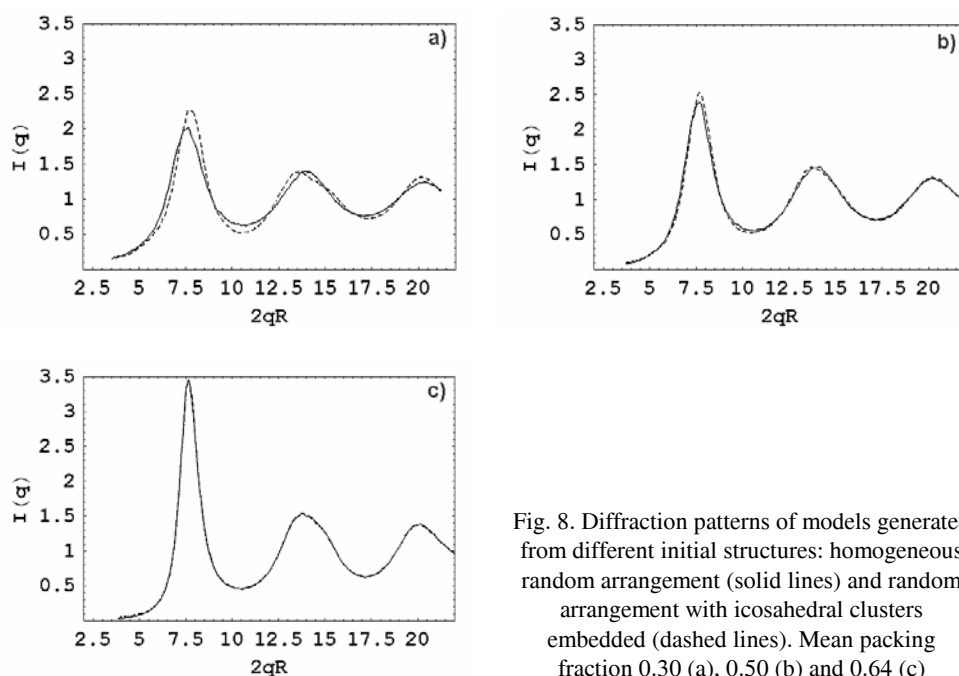

Fig. 8. Diffraction patterns of models generated from different initial structures: homogeneous random arrangement (solid lines) and random arrangement with icosahedral clusters embedded (dashed lines). Mean packing fraction 0.30 (a), 0.50 (b) and 0.64 (c)

The shoulder of the second maximum is well developed for the icosahedral system. This shoulder was discussed in [11] as a feature which is characteristic of structures with icosahedral short-range order and it was used in [2] for the interpretation of experimental curves obtained from liquid metals. The present model with icosahedral clusters in the initial structure still shows a bimodal distribution of local packing fraction at the mean packing fraction of 0.50 (Fig. 7b), but the difference of the corre-

sponding diffraction curve to that for the random system is very weak (Fig. 8b). At the mean packing fraction of 0.64 the diffraction curves of the two systems cannot be distinguished (Fig. 8c).

4. Discussion and conclusions

The simulations with equal spheres show that crystallization appears in hard sphere systems during densification above the global packing fraction of 0.64, which is characteristic of the standard dense-random packing model (for equal spheres). This confirms that there is no homogeneous random arrangement of hard spheres possible above 0.64, and models with higher values must be heterogeneous. The heterogeneity was realized in these simulations by mixtures of face-centred cubic nanocrystals of local packing fraction of 0.74 and the disordered (i.e., liquid or amorphous) matrix.

It was also expected that mixtures of amorphous matrix and icosahedral clusters would appear during densification but this was not the case. In previous papers [29, 30], the authors proposed the existence of icosahedral order with hard-sphere packing. However, the common-neighbour analysis done in [29] does not give an exact measure for icosahedrality and, furthermore, the amount of 13-sphere clusters having a central atom was negligible. In [30], a Voronoi analysis was carried out and the authors concluded that *the system approaches icosahedral order when increasing the density…* Indeed, they did not found any sphere in the systems analysed with the Voronoi cell volume required for local icosahedral order.

In the binary systems considered, the value 0.90 was chosen for the ratio of small to large spheres in order to favour and to stabilize local icosahedral arrangements. The result was that no icosahedra were formed during densification up to a mean packing fraction of 0.64. Instead, systems containing icosahedral clusters (13 atoms) in the initial state transform into a homogeneous disordered state without any icosahedron. It might be that there is a critical size of icosahedral arrangements which is above the size of the13-atoms clusters considered in the simulation. Such a critical size, which seems to exist for the fcc crystallites observed, may be controlled by the packing mis-fit at the interface between the cluster and the amorphous or liquid matrix.

The present study also showed that simulations of structural fluctuations on the nanometre scale are of interest for the interpretation of related experimental data.

References

[1] REICHERT H., KLEIN O., DOSCH H., DENK M., HONKIMÄKI V., LIPPMANN T., REITER G., Nature, 408 (2000), 839.

[2] SCHENK T., HOLLAND-MORITZ D., SIMONET V., BELLISENT R., HERLACH D.M., Phys. Rev. Lett., 89 (2002), 075507.

[3] FRANK F.C., Proc. Roy. Soc. London A, 215 (1952), 43.

[4] SPAEPEN F., Nature, 408 (2000), 781.

[5] Mattern N., Kühn U., Neuefeind J., Eckert J., Appl. Phys. Lett., 77 (2000), 1153.

[6] Fan C., Inoue A., Appl. Phys. Lett., 77 (2000), 46.

[7] Fan C., Li C., Inoue A., Haas V., Phys. Rev. B, 61 (2000), R3761.

[8] Hermann H., Heinemann A., Bauer H.-D., Mattern N., Kühn U., Wiedenmann A., J. Appl. Cryst., 34 (2001), 666

[9] Hermann H., Mattern N., Kühn U., Heinemann A., Lazarev N.P., J. Non-Cryst. Solids, 317 (2003), 91.

[10] Stadelmann P.A., Ultramicroscopy, 21 (1987), 131.

[11] Van De Waal B., J. Non-Cryst. Solids, 189 (1995), 118.

[12] Doye J.P.K., Wales D.J., Zetterling F.H.M., Dzugutov M., J. Chem. Phys., 118 (2003), 2792.

[13] Doye J.P.K., J. Chem. Phys., 119 (2003), 1136.

[14] Cozzini S., Ronchetti M., Phys. Rev. B, 53 (1996), 12040.

[15] Dzugutov M., Phys. Rev. A, 46 (1992), R2984.

[16] Dzugutov M., Phys. Rev. Lett., 70 (1993), 2924.

[17] Hui L., Guanghou W., Xiufang B., Feng D., Phys. Rev. B, 65 (2001), 035411.

[18] Hui L., Xiufang B., Guanghou W., Phys. Rev. B, 67 (2003), 094202.

[19] Wang L., Xiufang B., Yang H., Physics Lett. A, 302 (202), 318.

[20] Alfe D., Kresse G., Gillan M. J., Phys. Rev. B, 61 (2000), 132.

[21] Sachdev S., *Icosahedral Ordering in Supercooled Liquids and Metallic Glasses*, [in:] K. J. Strandburg (Ed.), *Bond Orientational Order in Condensed Matter Systems*, Springer-Verlag, New York, 1992.

[22] Clarke A.S., Wiley J.D., Phys. Rev. B, 35 (1987), 7350.

[23] Yang A., Miller C.T., Turcoliver L.D., Phys. Rev. E, 53 (1996), 1516.

[24] Jodrey W.S., Tory E.M., Powder Technol., 30 (1981), 111; Phys. Rev. A, 32 (1985), 2347; A 34 (1986), 675.

[25] Bezrukov A., Bargiel M., Stoyan D., Part. Syst. Charact., 19 (2002), 111.

[26] Torquato S., Truskett T.M., Debenedetti P.G., Phys. Rev. Lett., 84 (2000), 2064.

[27] Williams S.R., Snook I.K., Van Megen W., Phys. Rev. E, 64 (2001), 021506.

[28] Rintoul M.D., Torquato S., Phys. Rev. Lett., 77 (1996), 4198.

[29] Clarke A.S., Jonsson H., Phys. Rev. E, 47 (1993), 3975.

[30] Jullien R., Jund P., Caprion D., Quitmann D., Phys. Rev. E, 54 (1996), 6035.