MODEL ANGULAR DISTRIBUTION FUNCTIONS IN CA$_3$, CA$_4$ AND CA$_6$ STRUCTURAL UNITS OF GLASSY SYSTEMS

GRZEGORZ BERGMAŃSKI[1], SANDRO FELIZIANI[2], AND JAROSŁAW RYBICKI[1,3]

[1] Department of Solid State Physics,
Faculty of Technical Physics and Applied Mathematics,
Gdansk University of Technology, Narutowicza 11/12, 80-952 Gdansk, Poland
tuptus@kdm.task.gda.pl

[2] Istituto di Matematica e Informatica, Università di Camerino,
via Madonna delle Carceri, I-62032 Camerino (MC), Italia

[3] TASK Computer Centre, Narutowicza 11/12, 80-952 Gdansk, Poland

Abstract: We have calculated model partial angular distribution functions (pADFs) in CA$_3$, CA$_4$ and CA$_6$ structural units, *i.e.* an equilateral triangle with three vertical anions, A, and a central cation, C, a regular tetrahedron with four vertical anions, A, and a central cation, C and a square bipyramid with six vertical anions, A, and a central cation, C. The model pADFs were calculated employing a simple Monte Carlo procedure: the ions were being shifted at random within 3D spheres of radius r with uniform probability density and the AAA, ACA and CAA angles were calculated for each random configuration. Repeating the calculation $10^8 - 10^9$ times produced smooth probability densities for the angles' values. Conventional reference data so obtained can be applied to estimate the overall degree of deformation of the considered structural units in numerically simulated materials.

Keywords: structure of matter, disordered systems, short-range order, stochastic geometry

1. Introduction

Computer simulations are widely used to calculate the structure of matter at the atomic level. Thanks to the recent progress in molecular interactions and developments in computer technology, at present complex molecular systems can be simulated realistically. The most common simulation techniques are the molecular dynamics (MD) [1–8] and Monte Carlo (MC) [9, 10] methods. Simulation results usually include the Cartesian coordinates of all the particles (usually several thousand, but frequently much more) within the simulation box in each time-step of the numerical integration of equations of motion. The structure recognition and quantitative characterisation turns out to be a non-trivial task. The geometry of the nearest neigbourhoods of various

atomic species is referred to as the short-range order (SRO). The basic information on SRO in computer simulated materials is provided by partial Radial Distribution Functions (pRDF) and partial Angular Distribution Functions (pADF), related to the probability density of finding various interatomic distances and angles between chemical bonds. While pRDFs are usually calculated during the simulation itself, pADFs are usually calculated during post-processing the results, using the atomic configurations stored during the simulation.

In the first approximation, the pRDFs peaks, especially in crystals at moderate temperatures, can be approximated by Gauss' functions. However, in disordered systems simple approximation with symmetric functions is insufficient, since pRDFs exhibit a considerable degree of asymmetry, with a positive Fisher parameter. The function most commonly used to describe pRDFs quantitatively is a Γ-like function discussed in [11–13]. The usage of this function has turned out to be very convenient to characterize MD- or MC-simulated glasses [14–25].

In the structural analysis of computer-simulated solids, pADFs are usually studied to a much lesser extent than pRDFs. This is probably due to pADFs' being very difficult or even impossible to measure experimentally, reasonably detailed comparison with experimental data thus rendered impossible. pADFs are usually calculated from the simulated atomic configurations just to obtain the positions of dominant inter-bond angles and in most cases no significant effort to interpret detailed pADFs shapes is undertaken. In particular, as far as the authors are aware, no analytical expression has been proposed to describe pADFs' shape. In the present paper we make a first step towards quantitative characterisations of pADFs, providing conventional reference data that may be used in rough estimation of the disorder degree in several typical structural units occurring in computer-simulated materials.

pADFs are simply histograms of appearance of angles formed by two adjacent bonds. For a system containing two atomic species, we have six different pADFs: AAA, CAA, CAC, ACC, ACA and CCC. AAA labels the distribution of angles between two A-A bonds, whereas AAC – between adjacent AA and AC bonds, *etc.*

In this paper, we discuss probability densities of inter-edge angles for three randomly deformed basic structural units:

- a CA_3 unit (labelled Tr), *viz.* a flat equilateral triangle with three vertical anions, A, and a central cation, C, placed in the centre of the triangle,
- a CA_4 unit (labelled Tet), *viz.* a regular tetrahedron with four vertical A sites and one central C site placed in the centre of the tetrahdron, and
- a CA_6 unit (labelled Bip), *viz.* a square bipyramid with six vertical equidistant A sites and a central C site placed in the centre of the basal square.

Since we discuss CA_n structural units, only three relevant (AAA, CAA and ACA) angular distributions are to be considered.

The paper is organized as follows. In Section 2, we present our approach and show the probability densities for inter-edge angles in the above-mentioned randomly deformed structural units, *i.e.* the conventional Monte Carlo-generated reference data. In Section 3, we discuss central moments of the obtained probability distributions. In the concluding Section 4, we outline possible applications of the obtained reference data.

2. Monte Carlo generation of reference data

The actual displacements of atoms from their ideal positions are correlated in thermally vibrating units and simultaneously influenced in a complicated way by instantaneous configurations of neighbouring atoms. Thus, a realistic generation of various configurations is quite difficult and we shall use the simplest possible models of vertex displacement probibilities, *viz.* uniform distributions.

In order to obtain the probability density distributions of appearance of angles' values, the following Monte Carlo method has been applied. Regular CA_n ($n = 3, 4, 6$) structural units (as defined in the Introduction) were repeatedly distorted at random and the resulting distributions of the AAA, CAA and ACA angles' values were collected. In particular, the C site (central cation) position was either fixed (in Tr-F, Tet-F and Bip-F simulations) or moveable (in Tr-M, Tet-M and Bip-M simulations), assuming random positions around its ideal position. The sites were repeatedly shifted at random around their ideal positions according to a very simple rule, *viz.* a spatially uniform probability density within 3D spheres of a given radius, r (deformation
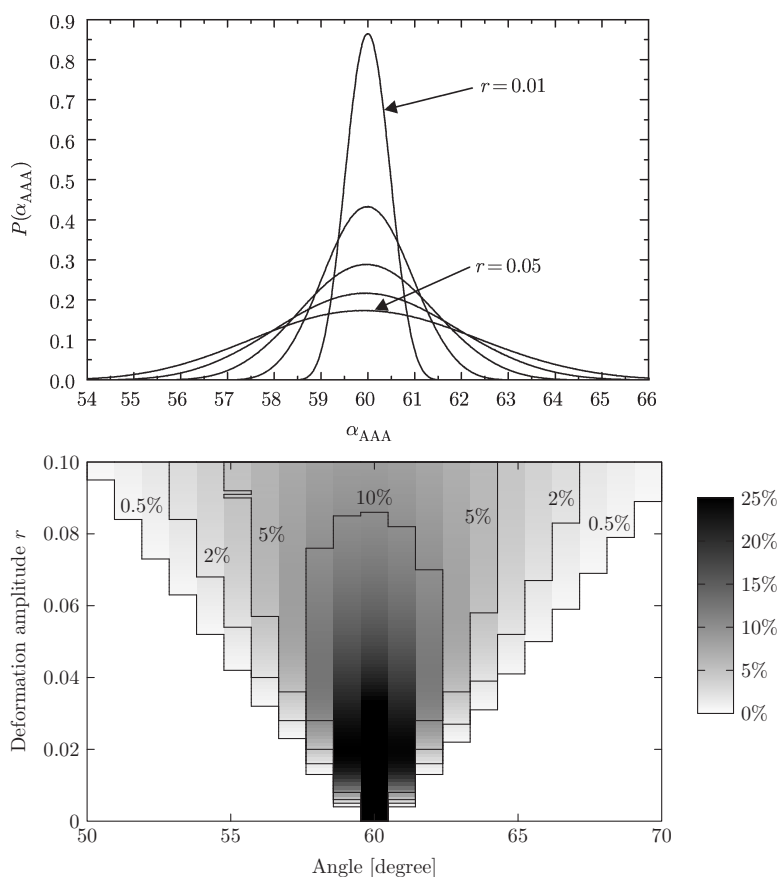
Figure 1. Top: Probability densities' distributions of appearance of AAA angles in a triangle of vertices (A sites) assuming random positions (with uniform probability) within spheres of radii $0 \leq r \leq 0.1$; the central C site remains fixed. Bottom: grey-scale representation of the same distributions calculated at the $\Delta r = 0.001$ step
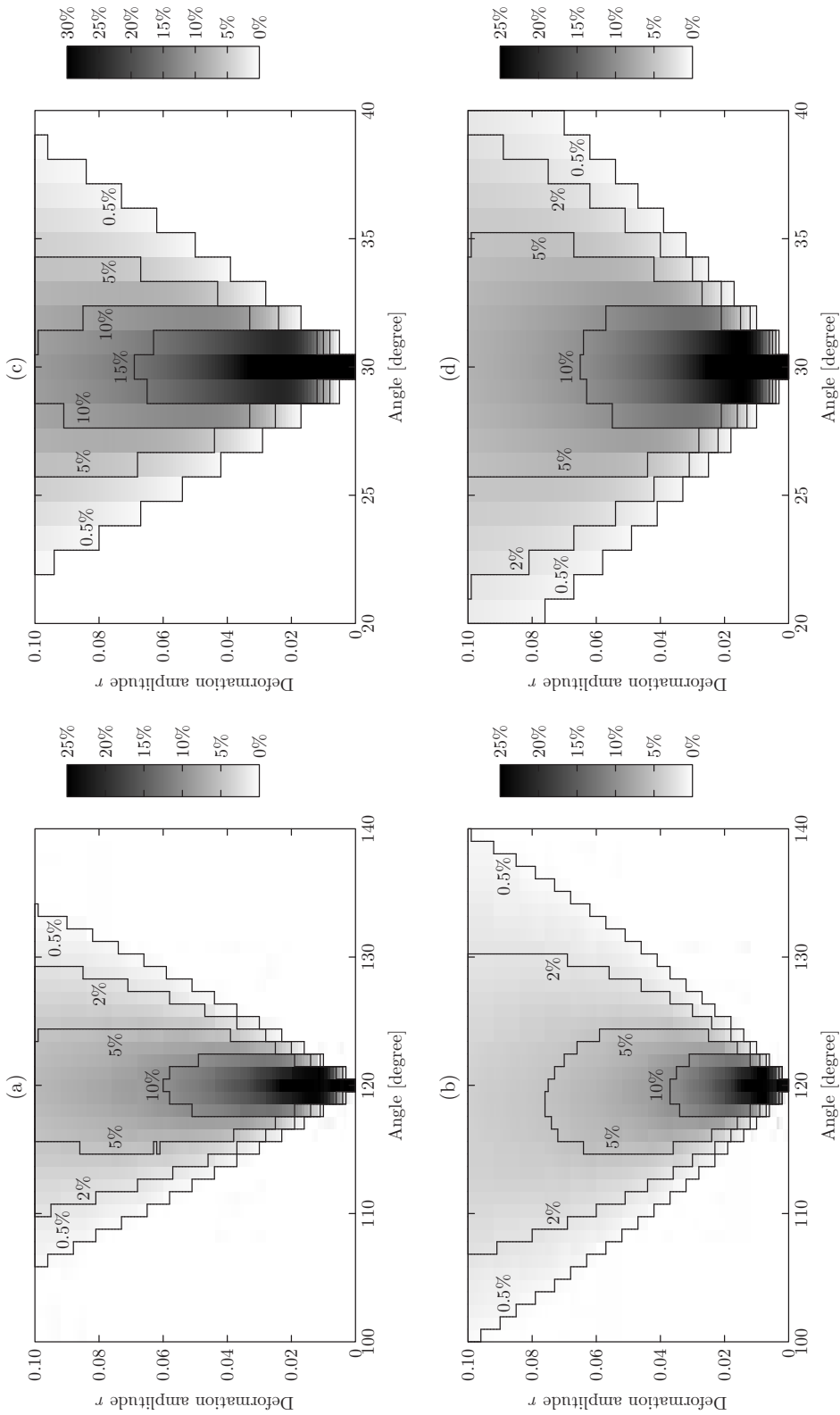
G. Bergmański et al.

Figure 2. Probability densities for ACA (a, b) and CAA (c, d) angles in Tr-F (a, c) and Tr-M (b, d)
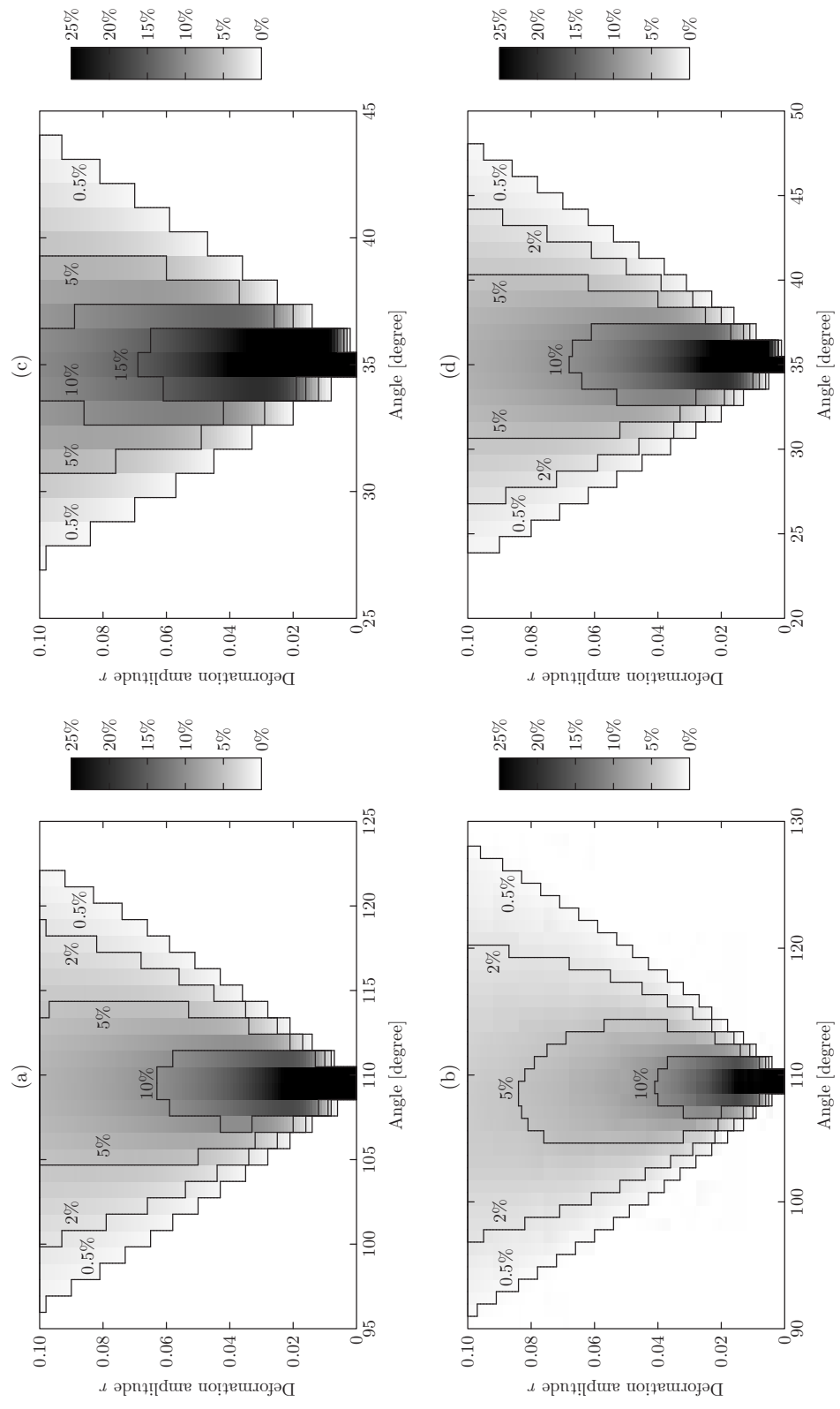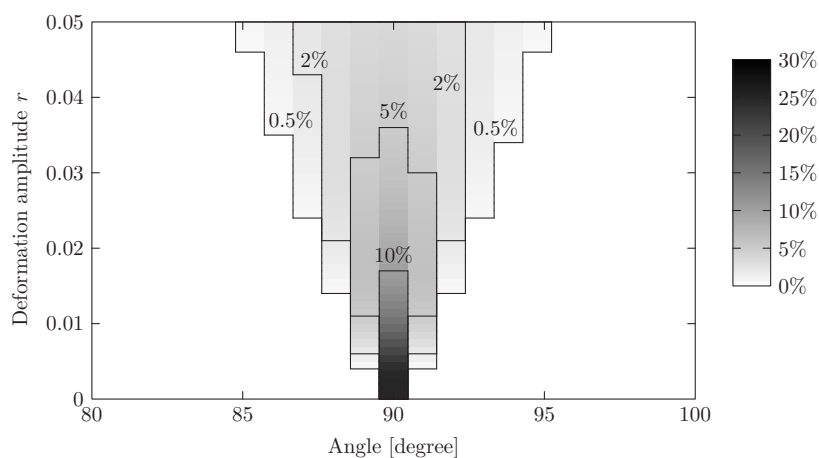
Figure 3. Probability densities for ACA (a, b) and CAA (c, d) angles in Tet-F (a, c) and Tet-M (b, d)

Figure 4. Probability densities for 90° AAA angles in Bip-F and Bip-M

amplitude). The A-A distance was set at 1 for all considered structural units, so that r could be interpreted as the vertex displacement amplitude proportional to the A-A distance. In order to obtain smooth probability distributions 10^8 or 10^9 deformed structures of each kind were generated. The calculations were performed for a series of deformation amplitudes, r, increasing from zero to 0.15.

The direct simulation results are histograms of appearence of angles' values for series of successive deformation amplitudes, r. The histograms have been normalized to one, *i.e.* they represent the probability density of finding a given values of angles.

Let us concentrate for a moment on the Tr-F simulation, where the C site remained immobile and the A vertices assumed random positions within spheres of radius r, centred at the ideal vertex positions (with uniform probability density in the spheres). Exemplary Monte Carlo results for the AAA angles' distributions for several values of r are shown in the left panel of Figure 1. Since similar distributions have been MC-simulated for r's in the range from 0 to 0.15 at a step of $\Delta r = 10^{-3}$, grey-scale maps have been created in order to show the results for all r radii. The map for the considered AAA-angle distribution is shown in the right panel of Figure 1. Here, the deformation amplitude increases along the vertical axis, while the angles' values increase along the horizontal axis. The intensity of the grey colour of pixels represents the probability density of finding an angle marked on the horizontal axis for deformation amplitudes, r, marked on the vertical axis. Contours have been added to guide the reader's eye, joining points of the same intensity of colour. Resolution along the horizontal axis is 1°.

The analogous data relative to the ACA and CAA angles in regular triangles, tetrahedra and square bipyramids are shown in Figures 2–5. The probability densities for the AAA angles equal to 60° are not shown, because they are the same as in Figure 1. All the reference data relative to pADFs can be found at http://www.task.gda.pl/nauka/software.
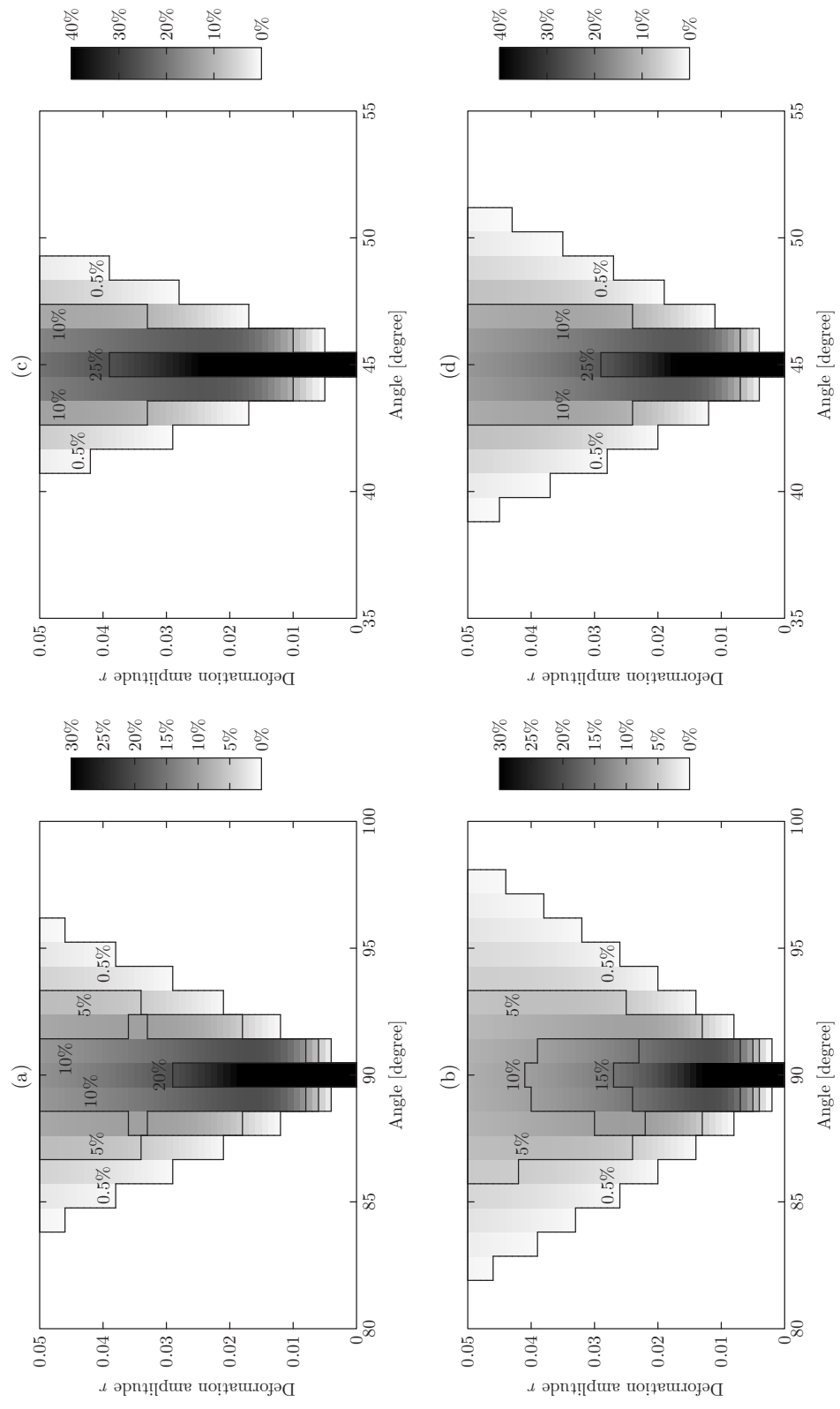
Figure 5. Probability densities for ACA (a, b) and CAA (c, d) angles in Bip-F (a, c) and Bip-M (b, d)

3. Statistical properties of inter-bond angle distributions

Let us consider central momenta known from elementary descriptive statistics. The arithmetic mean, $\overline{x}$, for frequency distribution f_i of finding values of x_i is defined as $\overline{x} = \sum_{i=1}^{k} x_i f_i / \sum_{i=1}^{k} f_i$, where k is the number of classes of x values. The variance of x is expressed as $\sigma^2 = \overline{x^2} - \overline{x}^2$ and measures the dispersion of values around the mean value. The distributions' shape can be characterized by a Fischer asymmetry coefficient, β, and a Pearson coefficient of curtosis, K:

$$\beta = \frac{\sum_{i=1}^{k}(x_i - \overline{x})^3 f_i}{\left(\sum_{i=1}^{k} f_i\right)\sigma^3}, \qquad K = \frac{\sum_{i=1}^{k}(x_i - \overline{x})^4 f_i}{\left(\sum_{i=1}^{k} f_i\right)\sigma^4}. \qquad (1)$$

The β parameter assumes null value for symmetric distributions. The greater the absolute value of β, the higher the degree of asymmetry. Positive and negative values of β respectively correspond to distributions with right and left asymmetry, respectively. The K parameter measures the deviation of a given distribution from the normal distribution. For exactly normal distributions one has $K = 0$. For $K \in (0,3)$ the analysed distribution is platicurtic, *i.e.* flatter than the normal distribution, while for $K \in (3,\infty)$ – it is leptocurtic, *i.e.* more peaked than the normal distribution.

The statistical parameters $\overline{\alpha}$, σ^2, β and K of distributions of the AAA, ACA and CAA angles are shown in Figure 6 in the function of the vertex displacement amplitude, r, for the Tr-F case. The corresponding graphs of all the remaining cases are very similar. In each case and to a very good accuracy, the mean values of the angles, their variances and curtosis parameters of the distributions are square functions of r ($\overline{\alpha}$, σ^2, $K = a + br^c$, $c = 2 \pm 0.01$), while the asymmetry coefficients are linear functions of r ($\beta = ar$). The cofficients' values are listed in Tables 1 and 2.

4. Conclusions

Having obtained a numerically-simulated structure of a material (*e.g.* from a molecular dynamics simulation), it is possible individuate structural units of a given type [25] and calculate for their angular distributions. However, it is difficult to extract quantitative information on the disorder degree from pADFs obtained in this way, and our reference data presented in Sections 2 and 3 can be useful in this respect: one can find a value of r, r_{min}, for which the difference between the reference distribution and a real MD-extracted pPDFs are minimized (*e.g.* in the minimum-square sense). Mean values, standard deviations and Fisher and Pearson parameters obtained for the reference data and those obtained from structural simulations can also be compared. Conclusions emerging from such comparisons may be that the overall deformation degree of a structural unit AC_n appearing in MD or MC structural simulation is effectively the same as that of the unit with fuzzy vertices, *i.e.* assuming random positions (with uniform probability density) within spheres of radius r_{min}. Thus, our procedure provides a conventional quantitative characterization of the deformation degree of basic structural units obtained in structural simulations.

Recently, several deformation degree estimators for CA_n units have been introduced by the present authors [26]. In [26], simlarly as in the present paper, a Monte Carlo method has been used to calculate the distributions of the estimators' values for various deformation amplitudes, r. Using such data, a minimum-square
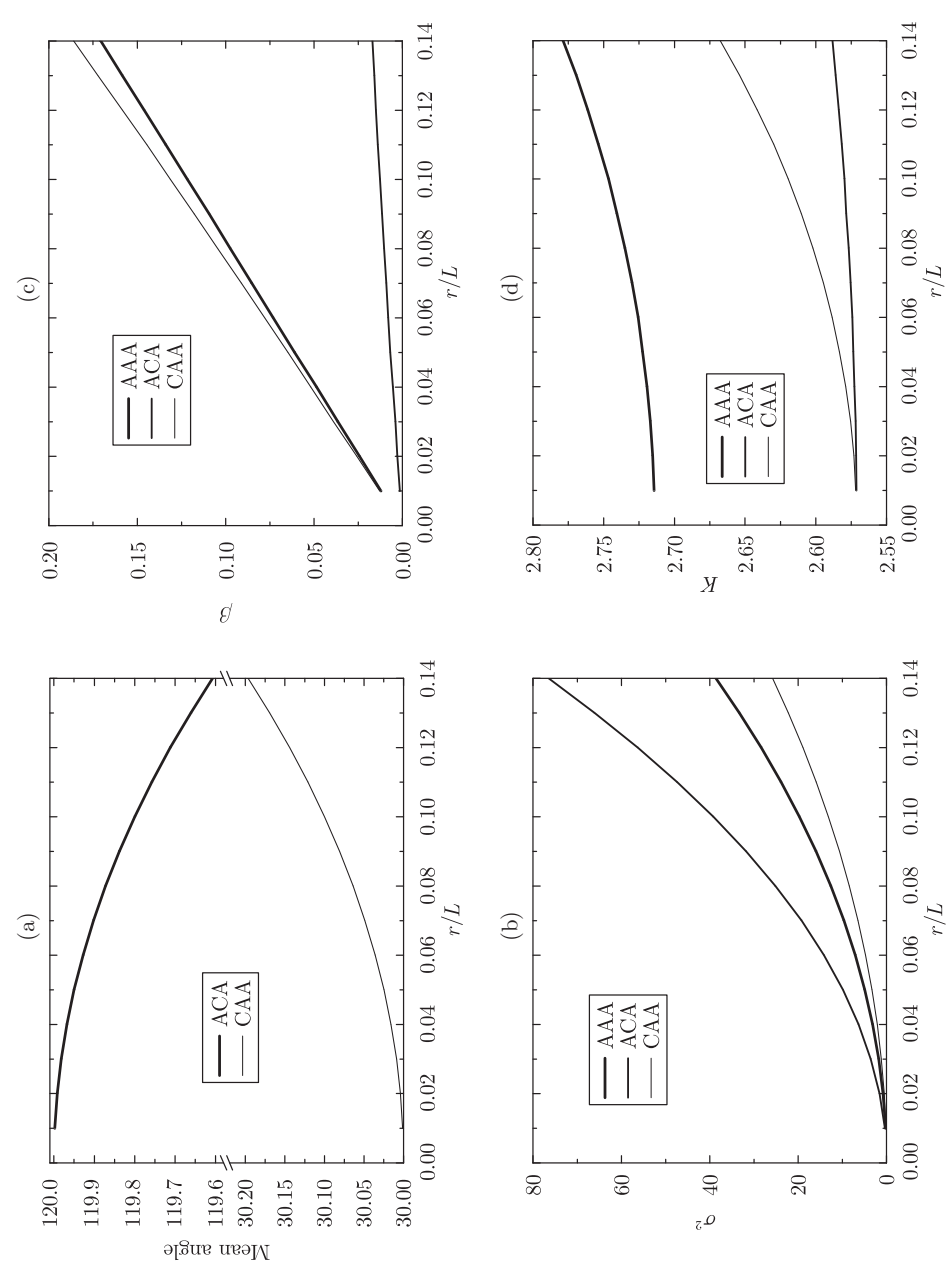
Figure 6. Central moments of probability densities for AAA, ACA and CAA angle distributions, the Tr-F case

Table 1. Coefficients of polynomials approximating the average angle values, variances, and Fisher and Pearson parameters in their dependence on r for Tr-F, Tr-M, Tet-F and Tet-M

	Tr-F	Tr-M	Tet-F	Tet-M
$\overline{\alpha}_{\mathrm{ACA}}$	$a=120,\ b=-20.4$	$a=120, b=-83.5$	$a=109.47,\ b=-11.0$	$a=109.47,\ b=-56.9.2$
σ^2_{ACA}	$a=0,\ b=3800$	$a=0,\ b=9300$	$a=0,\ b=3390$	$a=0,\ b=8100$
β_{ACA}	$a=0.12$	$a=1.70$	$a=0.07$	$a=1.79$
K_{ACA}	$a=2.57,\ b=0.87$	$a=2.62,\ b=3.41$	$a=2.57,\ b=0.71$	$a=2.64,\ b=5.01$
$\overline{\alpha}_{AAA}$	$a=60.0,\ b=c=0$	as for Tr-F	as for Tr-F	as for Tr-F
σ^2_{AAA}	$a=0,\ b=1970$	as for Tr-F	as for Tr-F	as for Tr-F
β_{AAA}	$a=1.22$	as for Tr-F	as for Tr-F	as for Tr-F
K_{AAA}	$a=2.71,\ b=3.43$	as for Tr-F	as for Tr-F	as for Tr-F
$\overline{\alpha}_{\mathrm{CAA}}$	$a=30.0,\ b=9.9$	$a=30.0,\ b=41.0$	$a=35.27,\ b=5.4$	$a=35.26,\ b=28.2$
σ^2_{CAA}	$b=1320$	$b=3180$	$b=1300$	$b=2990$
β_{CAA}	$a=1.34$	$a=0.85$	$a=1.50$	$a=0.98$
K_{CAA}	$a=2.57,\ b=5.02$	$a=2.62,\ b=6.35$	$a=2.57,\ b=5.30$	$a=2.64,\ b=5.79$

Table 2. Coefficients of polynomials approximating the average angle values, variances, and Fisher and Pearson parameters in their dependence on r for Bip-F and Bip-M

	Bip-F	Bip-M
$\overline{\alpha}_{\mathrm{ACA}=90}$	$a=90,\ b=-7.2$	$a=90, b=-45.0$
$\sigma^2_{\mathrm{ACA}=90}$	$a=0,\ b=3000$	$a=0,\ b=7600$
$\beta_{\mathrm{ACA}=90}$	$a=0.06$	$a=1.45$
$K_{\mathrm{ACA}=90}$	$a=2.60,\ b=0.70$	$a=2.40,\ b=0.65$
$\overline{\alpha}_{\mathrm{CAA}=45}$	$a=45.0,\ b=3.2$	$a=45,\ b=23.2$
$\sigma^2_{\mathrm{CAA}=45}$	$a=0,\ b=1220$	$a=0,\ b=2800$
$\beta_{\mathrm{CAA}=45}$	$a=1.62$	$a=0.94$
$K_{\mathrm{CAA}=45}$	$a=2.55,\ b=5.55$	$a=2.62,\ b=5.66$
$\overline{\alpha}_{\mathrm{AAA}=90}$	$a=90.2,\ b=2.8$	as for Bip-F
$\sigma^2_{\mathrm{AAA}=90}$	$b=1400$	as for Bip-F
$\beta_{\mathrm{AAA}=90}$	$a=1.60$	as for Bip-F
$K_{\mathrm{AAA}=90}$	$a=2.49,\ b=5.40$	as for Bip-F

method was used to fit the reference data to the related MD results in the best way, so obtaining the optimal value of r, $r_{\min}$. It could be concluded that the overall deformation degree of the considered structural AC_n units appearing in the MD-simulated materials was effectively the same as that of the unit with vertices occupying random position within spheres of radius r_{min} (with uniform probability density). The r_{min} parameters so determined for BO_3 triangles and SiO_4 tetrahedra in MD-simulated B_2O_3 and $PbOSiO_2$ glasses via analysis of the deformation degree estimators of [26] were 0.03 and 0.05, respectively [25].

In the present work, we have described analogical Monte Carlo-generated reference data concerning pADFs and proposed an analogical fitting procedure in order to characterize the degree of disorder quantitatively. The r_{min}'s obtained while analyzing the pADFs are again 0.03 and 0.05, respectively for BO_3 triangles and SiO_4 tetrahedra in B_2O_3 and $PbOSiO_2$ glasses (identical MD-simulated structures were submitted to both methods of analysis). This means that both approaches, *viz.* of [26] and of the present paper, are equally efficient in raw quantitative estimation of the disorder degree present in materials structures.

References

[1] Hoover W G 1986 *Molecular Dynamics*, Lecture Notes in Physics **258**, Springer-Verlag, Berlin, Heidelberg, New York

[2] Ciccotti G and Hoover W G (Eds) 1986 *Molecular Dynamics Simulation of Statistical Mechanical Systems*, Proc. Enrico Fermi Summer School, North Holland-New York

[3] Allen M P and Tildesley D J 1987 *Computer Simulation of Liquids*, Clarendon Press, Oxford

[4] Hockney R W and Eastwood J W 1987 *Computer Simulation using Particles*, McGraw-Hill

[5] Haile J M 1992 *Molecular Dynamics Simulation*, New York, John Wiley & Sons

[6] Rapaport D C 1995 *The Art of Molecular Dynamics Simulations*, Cambridge University Press

[7] Frenkel D and Smit B 1996 *Understanding Molecular Simulations: From Algorithms to Applications*, San Diego, London, Boston, New York, Sydney, Tokyo, Toronto

[8] Sadus R 1999 *Molecular Simulation of Fluids. Theory, Algorithms and Object-Orientation*, Elsevier, Amsterdam

[9] Binder K (Ed.) 1979 *Monte Carlo Methods in Statistical Physics*, Springer-Verlag, Berlin

[10] Binder K and Heerman D W 1988 *Simulation in Statistical Physics*, Springer-Verlag, Berlin

[11] Yang D S, Fazzini D R, Morrison T I, Tröger L and Bunker G 1997 *J. Non-Cryst. Solids* **210** 275

[12] Filipponi A and Di Cicco A 1995 *Phys. Rev.* **B 51** 12322

[13] Filipponi A 2001 *J. Phys. CM* **13** R23

[14] Rybicki J, Witkowska A, Bergmański G, Bośko J, Mancini G and Feliziani S 2001 *Comput. Meth. Sci. Technol.* **7** (1) 91

[15] Rybicki J, Rybicka A, Witkowska A, Bergmański G, Di Cicco A, Minicucci M and Mancini G 2001 *J. Phys. CM* **13** 9781

[16] Di Cicco A, Minicucci M, Principi E, Witkowska A, Rybicki J and Laskowski R 2002 *J. Phys. CM* **14** 3365

[17] Witkowska A, Murawski L and Bergmański G 2002 *TASK Quart.* **6** (2) 273

[18] Witkowska A, Rybicki J and Di Cicco A 2002 *Phys. Chem. Glasses* **43C** 124

[19] Rybicki J, Witkowska A, Bergmański G, Mancini G and Feliziani S 2003 *TASK Quart.* **7** 243

[20] Bergmański G, Białoskórski M, Rychcik-Leyk M, Witkowska A, Rybicki J, Frigio S and Feliziani S 2004 *TASK Quart.* **8** (3) 391

[21] Walentynowicz A, Witkowska A, Białoskórski M, Rybicki J and Feliziani S 2004 *Comput. Meth. Sci. Technol.* **10** 203

[22] Witkowska A, Rybicki J and Di Cicco A 2005 *J. Non-Cryst. Solids* **351** 380

[23] Witkowska A, Rybicki J and Di Cicco A 2005 *J. Alloys and Compounds* **401** 135

[24] Witkowska A, Madecka A, Trzebiatowski K, Dziedzic J and Rybicki J 2005 *Revs. Adv. Mat. Sci.* **12** 112

[25] Bergmański G 2006 *Structural Analysis of Computer-Simulated Materials*, PhD Thesis, Gdańsk University of Technology, Gdańsk (in Polish)

[26] Bergmański G, Białoskórski M, Rybicki J and Feliziani S 2005 *phys. stat. sol.* (b) **242** 519