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Structure recognition in MD-simulated materials. A case study of BO_3 triangles in borate glasses

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In computer simulations of the structure of matter, one usually obtains the Cartesian coordinates of all the particles involved. A non-trivial problem of structure recognition and characterization arises. In the present contribution, we study in detail the geometrical properties of a fuzzy-vertex CA_3 structural unit (C – cation, A – anion). Two deformation degree estimators are introduced and examined. The Monte Carlo-generated stochastic characteristics of fuzzy CA_3 triangles constitute conventional reference data that can be compared with the corresponding distributions calculated for a computer-simulated material. A quantitative estimation of the deformation degree of CA_3 units in the simulated structure can thus be obtained. We apply the methods developed to quantitatively characterize the geometry of BO_3 structural units in B_2O_3 glass.

Key words: *short-range order; shape parameters; molecular dynamics; borate glass*

1. Introduction

Computer simulations are widely used to calculate the structure of matter at the atomic level. The most common techniques are molecular dynamics (MD, e.g. [1–3]) and Monte Carlo (MC, e.g. [4, 5]) methods. At present, one can simulate fairly large systems, containing up to about 10^9 particles. Up to the date, structures of thousands of various materials have been simulated, including functional materials, very complex in their structure and behaviour. Computer technology development itself, however, does not automatically guarantee sufficiently good reliability of the simulation results. Even for relatively simple materials one encounters enormous difficulties in reproducing their correct structure.

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The result of a direct MD simulation is a set of the Cartesian coordinates (and velocities) of all the particles versus time. A non-trivial problem of structure recognition arises. As far as the short-range ordering in the simulated material is concerned, it is often sufficient to analyse partial pair distribution functions (pPDF) together with angular distribution functions[*]. The detected structural units are often claimed vaguely to be more or less distorted, usually with little effort to provide a precise, quantitative characterization of the degree of distortion.

In the present contribution, we make a step towards the development of tools allowing a conventional quantitative characterization of the deformation degree of simple structural units appearing in computer-simulated material structures. We study in detail geometrical properties of a CA_3 structural unit (C – cation, A – anion), i.e. of a flat equilateral triangle with three anions in its vertices and a cation in the triangle's centre. In particular, we use the Monte Carlo method to obtain the distributions of AAA, ACA, and CAA angles in a fuzzy-vertex CA_3 unit, i.e. with random positions of anions, assumed to have uniform probability densities within spheres of radius r (the deformation amplitude), centred on the ideal vertex positions. We scan the interval $0 < r \leq r_{max}$, r_{max} being equal to 10% of the AA distance, with the step of 0.001. Moreover, two deformation degree estimators are introduced (cf. [12]), and the distributions of their values as functions of the deformation amplitude r are calculated. The MC-generated distributions constitute conventional reference data (obtained for a non-interaction purely stochastic geometry model) that can be compared with the corresponding distributions calculated for a computer-simulated material. A quantitative estimation of the deformation degree of CA_3 units in the simulated structure can thus be obtained. We apply the developed methods to quantitatively characterize the geometry of BO_3 structural units in B_2O_3 glass, simulated using an MD technique with three various inter-atomic potentials, each of them adequately reproducing the experimental short-range correlations. We show that the degree of deformation of the basic structural units appear to be highly potential-dependent.

Although B_2O_3 glass has been known for many years and has found numerous important practical applications (e.g., in optical fibre technology), its structure is still intensively studied, and several questions and doubts on B_2O_3 structure remain open. Goubeau and Keller [13] suggested that B_2O_3 glass consists of planar hexagonal B_3O_3 boroxyl rings interconnected by bridging oxygen atoms. Although Krogh-Moe [14] showed that several properties of borate glass are consistent with this model, its uniqueness has not been proven, and the existence of boroxyl rings has been seriously questioned. There is strong evidence from nuclear magnetic resonance (NMR) studies that each B atom is at the centre of an equilateral triangle having oxygen atoms in its corners [15]. Mozzi and Warren [16] have found their X-ray-extracted radial distribution functions to be fitted better by a model in which most of these triangles are or-

[*]There are other ways to characterise the local structure, such as the Voronoi polyhedra or Delunay simplexa techniques [6–11].

dered in flat boroxyl rings. Elliott [17] has calculated pPDFs from computer-simulated structures and concluded that the X-ray data can be better understood by a continuous random network (CRN) of BO_3 triangles (no boroxyl rings). In the opinion of Galeener et al. [18], borate glasses reveal fractions of both of the above-mentioned structural features. More recently, Swenson and Borjesson [19], using the reverse Monte Carlo modelling, have argued that a fraction of BO_3 triangles form deformed (not flat) boroxyl rings.

The paper is organized as follows. In Section 2, we investigate the stochastic geometry properties of fuzzy CA_3 structural units. In Section 3, we describe our MD simulations of B_2O_3 glass and apply the developed tools to analyse the structure of BO_3 units. Section 4 contains concluding remarks.

2. Geometric properties of fuzzy CA_3 triangles

The actual displacements of atoms from their ideal positions are correlated within a thermally vibrating unit and influenced in a complicated way by the instantaneous configurations of neighbouring atoms. Thus, the realistic generation of reference data is quite difficult and we have used a very simple, non-interaction model of vortex displacements, viz. a uniform probability distribution within a sphere centred on the ideal (equilibrium) anion position.

An equilateral triangle with the fourth site in its geometrical centre was repeatedly distorted at random: vortices were shifted at random within spheres of radii equal to a fraction r of the ideal AA distance, whereas the C-site position remained fixed. 10^7 distorted polyhedra were generated in order to calculate the distributions of the AAA, ACA, and CAA angles and the distortion parameters, Tr_1 and Tr_2 (defined below). Such Monte Carlo calculations were performed for a series of subsequent values of r, varying with a step of $\Delta r = 0.001$ from zero to $r_{max} = 0.1$ of the AA distance. The AAA, ACA, and CAA angular distributions in fuzzy-vertex CA_3 units for several values of the deformation amplitude r are shown in Figure 1.

Let us consider the central tendencies of the AAA, ACA, and CAA angular distributions. The arithmetic mean $\overline{x}$, for the frequency distribution f_i of finding values of x_i is defined as $\overline{x} = \sum_{i=1}^{k} x_i f_i \Big/ \sum_{i=1}^{k} f_i$, 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 the distribution values around the mean value. The shape of the distributions shape can be characterised by the Fischer asymmetry coefficient β and the Pearson coefficient of kurtosis K:

$$\beta = \frac{\sum_{i=1}^{k} \left(x_i - \overline{x}\right)^2 f_i}{\left(\sum_{i=1}^{k} f_i\right)\sigma^3}, \qquad K = \frac{\sum_{i=1}^{k} \left(x_i - \overline{x}\right)^4 f_i}{\left(\sum_{i=1}^{k} f_i\right)\sigma^4} \tag{1}$$

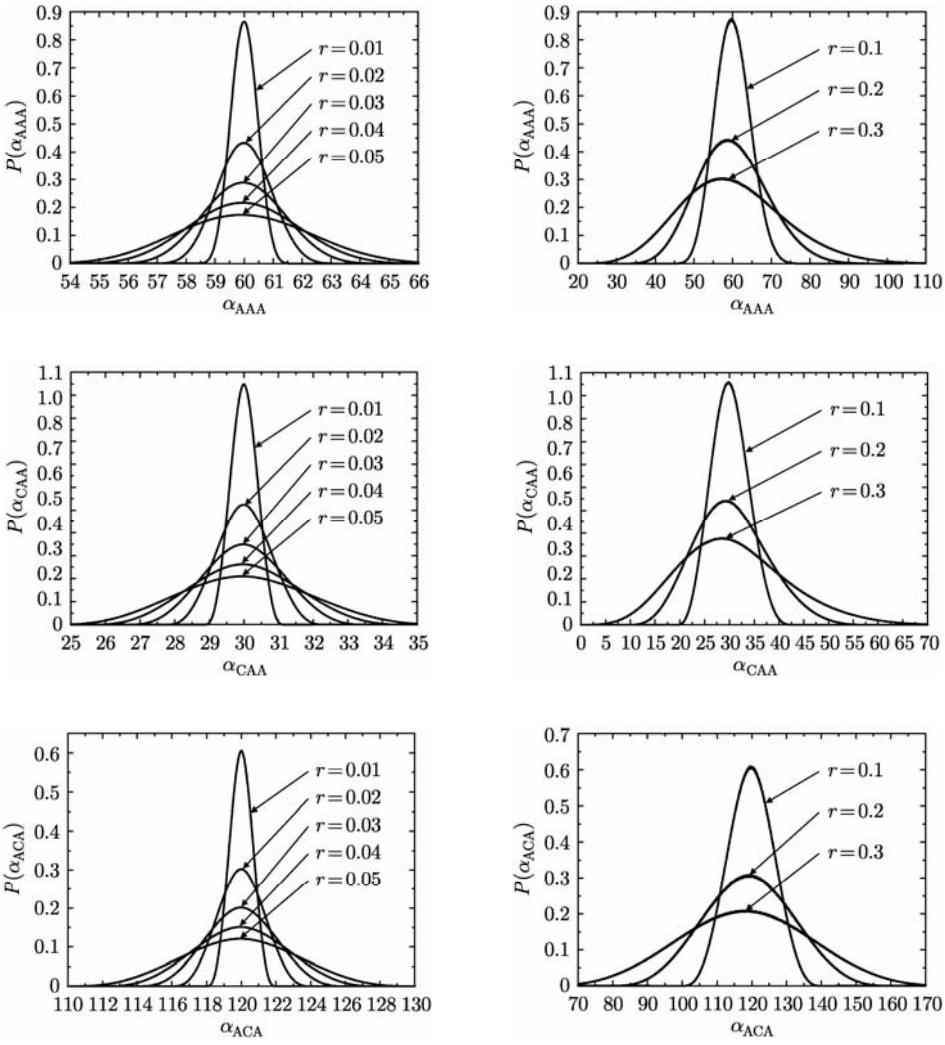

Fig. 1. Probability densities $P(\alpha)$ for the AAA, CAA, and ACA angular distributions

The β parameter is zero for symmetric distributions. The higher the absolute value of β, the higher is the degree of asymmetry. Positive and negative values of β correspond to distributions with a right and left asymmetry, respectively. The K parameter measures the deviation of a given distribution from the normal distribution. For exactly normal distributions, $K = 3$. 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 leptokurtic, i.e. more peaked than the normal distribution. The r-dependences of the mean values of the AAA, ACA, and CAA angular distributions, their variances, and Fisher and Pearson parameters are shown in Figure 2.

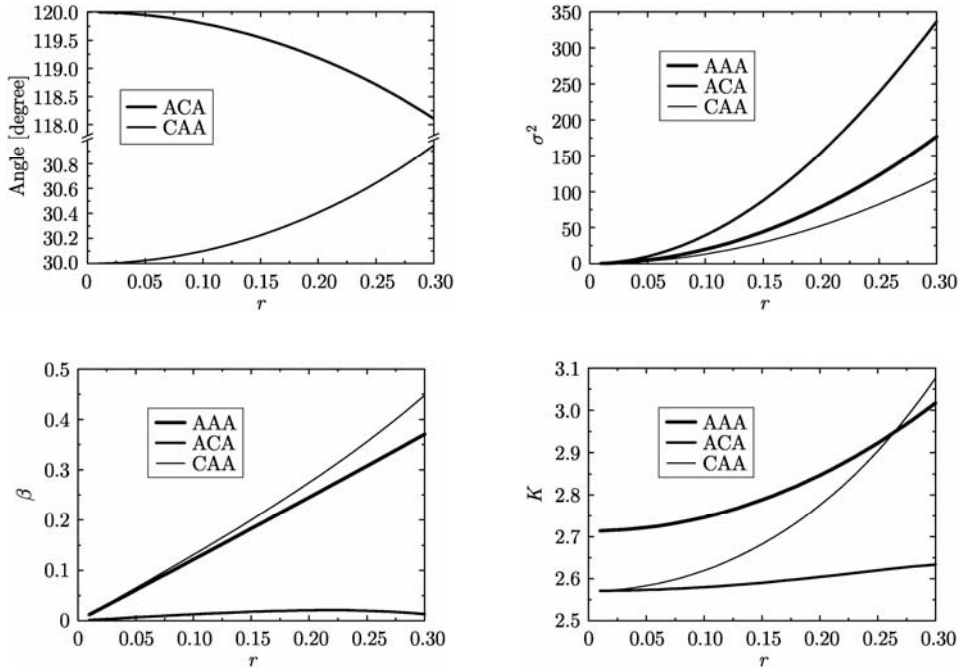

Fig. 2. Central tendencies of the probability densities $P(\alpha)$ for the angular distributions AAA, ACA and CAA for which vertices (A-sites) assume random positions within 3D spheres with uniform probability. Upper left: mean angle, upper right: angle variance, lower left: the Fischer asymmetry coefficient β, lower right: the Pearson coefficient of kurtosis K. The mean value of the AAA angle is r-independent and equal to 60°

In order to measure the overall degree of deformation of CA_3 triangles, we define two estimators (cf. [12]):

$$Tr_1 = \frac{\sum_{i=1}^{3}(\bar{l}_{A-A} - l_{A-A,i})^2}{3\bar{l}_{A-A}^2} \tag{2}$$

and

$$Tr_1 = \frac{\sum_{i=1}^{3}(\bar{l}_{A-A} - l_{A-A,i})^2}{3\bar{l}_{A-A}^2} + \frac{\sum_{i=1}^{3}(\bar{l}_{C-A} - l_{C-A,i})^2}{3\bar{l}_{C-A}^2} \tag{3}$$

where $\bar{l}_{A-A}$ and $\bar{l}_{C-A}$ denote the average AA and CA distances, whereas $\bar{l}_{A-A,i}$ and $\bar{l}_{C-A,i}$ the actual lengths of the i-th AA sides and CA distances, respectively. The above deformation estimators are zero for a regular (ideal) geometry and positive for deformed structures. MC simulation results for the CA_3 unit are shown in Figure 3.

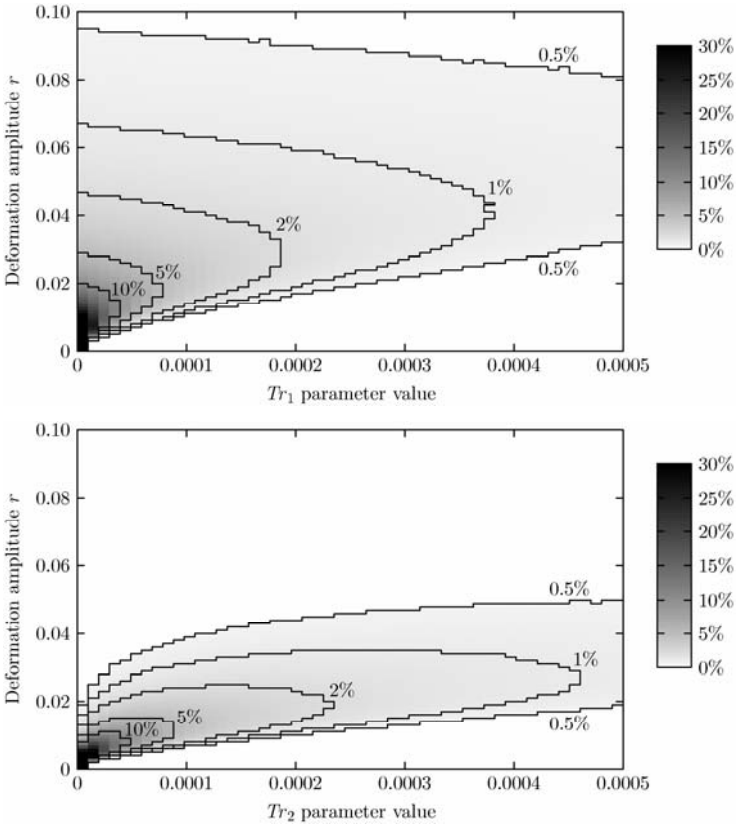

Figure 3. Distributions of Tr_1 and Tr_2 parameter values in the function of the anion shift amplitude

In order to see whether the CA_3 triangles are flat, a simple additional parameter, $\bar{H}$, has been introduced. $\bar{H}$ is defined as the average distance from the central cation to the plane spanned by the three neighbouring anions. The lower $\bar{H}$ is, the flatter the CA_3 unit. The dependences of $\overline{Tr}$ and $\sigma^2(Tr)$ are shown in Figure 4. The mean values of the distributions of Tr_1 and Tr_2 depend on r approximately quadratically, i.e. as ar^{α}, where α is close to 2 (up to about 0.01), whereas the coefficient a assumes the values of 0.20 and 0.58 for Tr_1 and Tr_2, respectively. The variances follow a cr^{γ} dependence with γ close to 4 (up to about 0.03), while the coefficient c equals 0.03 and 0.18 for Tr_1 and Tr_2, respectively. The r-dependences of β and K are linear:

$$\beta_{Tr1} = 0.72 + 0.35r, \qquad K_{Tr1} = 3.50 + 0.32r$$

$$\beta_{Tr1} = 0.52 + 0.40r, \qquad K_{Tr2} = 3.21 + 0.66r$$

The mean value of the parameter H related to CA_3 triangles, $\bar{H}$, also depends linearly on r, according to $\bar{H}(r) = 0.21r$, where 0.21 is an empirical MC coefficient.

Having a numerically simulated structure of a particular material at one's disposal (in the present case, B_2O_3 glass structure from a molecular dynamics simulation), it is possible to calculate the values of estimators and angles for all the BO_3 units detected within the simulation box and construct the corresponding histogram of the occurrence frequencies of these values. Data obtained in this way, however, are difficult to interpret quantitatively. In order to enable such an interpretation, the properties of the angular distributions and deformation degree estimators were studied separately (independently of any physical system), providing reference data, which is presented in proceeding paragraphs. A comparison of the distributions of estimators and angles for a given numerically simulated material with the above reference makes it possible to quantitatively characterize the degree of disorder in a material structure obtained from a simulation.

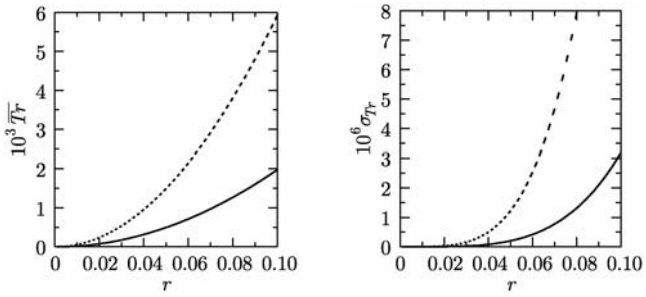

Fig. 4. The r-dependence of the distributions $\overline{Tr}_1$ and $\sigma^2(Tr_1)$ (solid lines) as well as $\overline{Tr}_2$ and $\sigma^2(Tr_2)$ (dashed lines)

A quantitative evaluation of the deformation degree of the simulated CA_3 triangles can be realised in the following steps:

- Calculating the distribution (histogram) of the values of estimators and angles for all the structural units detected in a numerically generated solid (i.e., for the MD simulation, the results of which are to be analysed). For this distribution, one can calculate its average value, standard deviation, asymmetry parameters (e.g. the Fisher parameter), and the Pearson kurtosis parameter.
- Minimum-square fitting of the Monte Carlo-generated distributions of estimators and angles (with the reference data described above) to the corresponding distribution obtained from a structure simulation yields the optimal value of r, $r_{\min} = q$. Mean values, standard deviations, and the 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_3 appearing in our MD structural simulation is effectively the same as that of the unit with fuzzy vertices, i.e. assuming random positions within spheres of radius q (with a uniform probability density). Thus, our procedure provides a conventional quantitative characterization of the deformation degree of basic structural units obtained in structural simulations.

3. BO_3 units in borate glasses – results of the simulation and discussion

Our MD simulations of borate glasses have been performed in the microcanonical ensemble (NVE) using the *mdsim* code [20]. The number of atoms within a cubic simulation box with periodic boundary conditions amounted to 5000. The glasses of 1800 kg/m^3 density were initially prepared in a well equilibrated molten state at 10 000 K, then cooled down to 300 K at an average rate of $2 \cdot 10^{13}$ K/s, passing equilibrium states at 8000 K, 6000 K, 5000 K, 4000 K, 3000 K, 2500 K, 2000 K, 1500 K, 1000 K, and 600 K. Temperature scaling was applied whenever the rolling average of temperature (calculated over the last 100 time steps) went out of the $(T - \Delta T, T + \Delta T)$ interval. At each intermediate temperature, the system was equilibrated during 30 000 fs time steps, using $\Delta T = 100$ K for $T \geq 1000$ K, $\Delta T = 20$ K for $T = 600$ K, and $\Delta T = 10$ K for 300 K. Equilibrated systems were sampled during 10 000 fs time steps.

Three various force field models were applied: that of Takada et al. [21, 22] (I), Xu et al. [23] (II), and Soules [24] (III). All the above-cited interaction potentials are of the Born–Meyer–Huggins type (with full ionic charges) and have been parameterised to reproduce the short-range structure inferred from experimental investigations.

One can calculate the angular OOO, OBO, and BOO distributions and the distributions of the parameters Tr_1 and Tr_2 (and various characteristics of the obtained distributions, such as central tendencies and standard deviation) for MD-simulated structures. For a complete quantitative analysis, however, one should compare the MD-extracted data for BO_3 triangles with the reference data presented in Section 2.

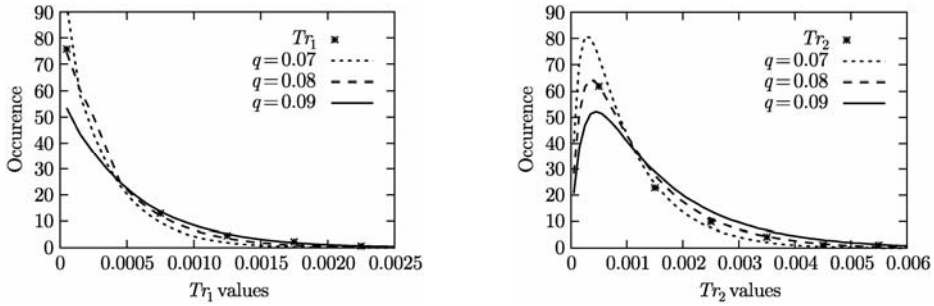

Fig. 5. Example MD-extracted distributions of the Tr_1 and Tr_2 parameters (potential (I) simulation), compared with the best-fit (q = 0.08) model Monte Carlo reference data. The Monte Carlo reference data for r = 0.07 and r = 0.09 are shown for comparison

Cation–anion adjacency graphs have been constructed with a cut-off distance on the B–O bond length equal to R_{cut} = 1.87 A, common to all the simulations. In the final structures obtained with force field (I), 99.9% of the B atoms have a three-fold oxygen co-ordination, whereas the (II) and (III) force fields produced structures with 97.75% and 99.6% of the B cations with three oxygen neighbours, respectively. Shape analysis has been performed on all of the BO_3 triangles found.

The analysis of the distributions of the Tr_1 and Tr_2 parameters consisted of their calculation for all the BO_3 triangles found in the simulated atomic configurations and of a minimum-square fitting to the Monte Carlo-generated reference data. In Figure 5, we have shown an example of MD-extracted distributions of the parameters Tr_1 and Tr_2 (for potential (III)), compared with the best-fit Monte Carlo reference data.

BO_3 units are the most deformed in structures obtained using potential (I) (the best-fit *r*-value, $q = 0.08$, $\bar{H} \approx 0.07$ Å). The most regular BO_3 triangles were obtained with interaction model (II) ($q = 0.03$, $\bar{H} \approx 0.05$ Å). Interaction model (III) yielded rather irregular BO_3 units, with $q = 0.045$ and $\bar{H} \approx 0.07$ Å.

All of the $\bar{H}_{MD}$ values have been compared with theoretically calculated $\bar{H}_{MC} = 0.21q$ values (Monte Carlo reference data). For all the cases, the $\bar{H}_{MD}$ values exceeded significantly the corresponding $\bar{H}_{MC}$ values. This means that the distance of B atoms from the oxygen plane is due to a structural deformation (low BO_3 pyramids) rather than from oxygen thermal vibrations of the flat BO_3 triangle.

Table 1. The *q* values obtained from fitting the Monte Carlo reference data of the angular distribution functions and the Tr_1 and Tr_2 parameters to the MD data obtained with potentials (I), (II), and (III). The fitting error does not exceed 0.005

Potential	OOO angles	OBO angles	BOO angles	Tr_1	Tr_2
(I)	0.07	0.08	0,07	0.08	0.08
(II)	0.02	0.03	0.03	0.03	0.03
(III)	0.05	0.05	0.05	0.04	0.05

The angular distribution functions for OOO, OBO, and BOO triples were also calculated for the MD-simulated structures and compared with the reference MC data. The best-fitting procedure yielded the *q* values listed in Table 1. Almost the same deformation amplitudes can be inferred by comparing the MD data with Monte Carlo reference data of the Tr_1 and Tr_2 parameters or of the AAA, ACA, and CAA angular distributions (A = O, C = B).

4. Concluding remarks

In this brief contribution, we have made a step towards developing useful tools that allow a conventional quantitative characterization of the deformation degree of the simple structural unit CA_3, which often appears in computer-simulated material structures. We have presented Monte Carlo reference data relative to angular AAA, ACA, and CAA distributions and deformation estimator value distributions in fuzzy vertex CA_3 triangles. The usefulness of MC reference data for characterising the degree of deformation of BO_3 structural units in MD-simulated B_2O_3 glass is demonstrated.

In MD simulations realised with three different parameterisations of the Born-Meyer-Huggins potential, almost all B atoms are at the centre of an equilateral triangle having an oxygen atom at each corner. A comparison of the MD-simulated OOO, OBO, and BOO angular distributions and distributions of the deformation estimator values with reference MC data for fuzzy vertex CA_3 triangles yielded the following quantitative characteristics for BO_3 units in borate gasses. The most regular BO_3 triangles were obtained using interaction model (II) ($q \approx 0.03$, $\bar{H} \approx 0.05$ A), less regular for interaction model (III) ($q \approx 0.045$, $\bar{H} \approx 0.07$ A), and the most distorted units were obtained for potential parameters (II) ($q \approx 0.08$, $\bar{H} \approx 0.07$ A). Such a high value of $\bar{H}$ for all potentials was classified as structural deformation, as $\overline{H_{MD}} > \overline{H_{MC}}$. The results described above mean that the overall deformation degrees of a structural unit BO_3 appearing in our MD structural simulation are effectively the same as for the unit with fuzzy vertices, which assumes random positions (with uniform probability density) within spheres of radii equal to 8%, 3%, and 4.5% of the mean OO distance for force fields (I), (II), and (III), respectively. Finally, it should be noted that the overall deformation degree of the BO_3 units inferred from the analysis of angular distributions and from the *Tr* estimator distributions are essentially the same, therefore practically it is sufficient to analyse only the angular correlations or deformation estimator distributions.

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