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ON PROBLEMS OF RELAXED COMPUTER MODELS OF THE STRUCTURE OF METALLIC GLASSES

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Some recent results in the modelling of the structure of metallic glasses are briefly reviewed. The importance of the usage of the realistic interatomic potentials is emphasized. The possibility of the evaluation of the potentials from the second equation of the BBGKY hierarchy is studied. To do so, a certain kernel of the integral equation must be known. The computer model of glassy $Ni_{81}B_{19}$ is constructed and the simple method of computing this kernel from the model exactly is derived. The approximation of this kernel based on the superposition approximation of the triplet correlation function and its true form calculated from the model are compared. The results show that with the exception of distances below the position of the first minimum of the pair correlation function this approximation is very good.

О ПРОБЛЕМЕ РЕЛАКСАЦИОННОГО МОДЕЛИРОВАНИЯ СТРУКТУРЫ МЕТАЛЛИЧЕСКИХ СТЕКОЛ ПРИ ПОМОЩИ ЭВМ

В работе приводится краткий обзор некоторых достижений в моделировании структуры металлических стекол. Подчеркивается необходимость использования в расчетах реалистических межатомных потенциалов и изучена возможность определения этих потенциалов из второго уравнения в цепочке уравнений ВВГКИ, для чего необходимо знать ядро некоторого интегрального уравнения. При помощи ЭВМ создана модель металлического стекла $Ni_{81}B_{19}$ и приводится простой точный метод, который позволяет определить из модели ядро интегрального уравнения. Проведено сравнение приближения для этого ядра, полученное на основе приближения функции тройной корреляции, с точным значением ядра, определенным из модели.

Результаты сравнения показывают, что данное приближение является хорошим за исключением расстояний, которые ниже первого минимума функции двойной корреляции.

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I. INTRODUCTION

In spite of a considerable effort the problem of the atomic structure of metallic glasses is not solved completely yet. Probably the most frequent way to study this structure is the computer modelling [1]. Computer models constructed by the relaxation, e.g. by the minimization of the total potential energy of the system when prescribed interatomic potentials are used, reproduce quite well the experimental data, although some differencies remain [2, 3, 4].

The main problems in the modelling could be divided into three groups. First, it is the reproducibility of models, e.g. that certain statistical characteristics which we use as criteria must be independent of the "technical" details of the relaxation (the type of minimization method, the number of atoms in the model, etc.). Recently Lancon et al. [5] have published a study of this question and as criteria they have used the pair correlation function (PCF), potential energy and density. Constructed models were one-component, with the Lennard-Jones interatomic potential. Their results showed that the change of number of atoms or the use of different boundary conditions (free, periodic) caused negligible differencies of the mentioned statistical characteristics. Also the usage of different methods of the minimization yielded only small changes of these characteristics.

The second problem is the question of the initial and terminal states, e.g. what and how many different glassy states (different in a sense of the above mentioned criteria) could be obtained when the relaxation is started from the different initial configurations. Very recently Lancon et al. [5, 6] have investigated the relaxation of the various initial disordered and partially ordered configurations. Using their results it is possible to propose a qualitative solution of this problem in the onecomponent system with the Lennard-Jones potential (Fig. 1). Every point of the horizontal axis represents the structure with a certain degree of disorder. The degree of disorder is increasing from left to right: C-crystal, A-amorphous state, D-"totally" disordered state. The state D is for example the structure created by the random number generator with an uniform distribution. When we take into account that the minimization methods are based on the gradient of the potential energy [2, 3, 4], it is clear that if the initial structure is somewhere between C and P after relaxation the crystalline order is obtained. Similarly, when the initial configuration is somewhere between P and D, the reproducible amorphous structure A is obtained, which, as it seems, is unique [5, 6]. Unfortunately, the situation is probably more complicated when the system is multicomponent or when more realistic potentials are used.

Thirdly there is the fundamental problem of the estimation of the true pair potentials. Very often the potentials are of the Lennard-Jones or the Morse types with the parameters estimated intuitively or fitted to some limited experimental information (elastic constants, isothermal compressibility, etc.). There are two

possible ways which yield the correct estimation of the potentials. The first is based on the ab initio quantum mechanics calculations. In fact, this approach is possible only for simple metals, but not for transition metals, because of a lack of the appropriate method [7]. Another approach are the BBGKY integral equations (the Bogolyubov—Born—Green—Kirkwood—Yvon hierarchy [8, 9]) from statistical mechanics, although this approach is also far from simple. The first disadvantage is the necessity of precise experiments which yield the PCF (or the partial pair correlation functions when the system is multi-component [10]). The other is the necessity of approximating the triplet correlation function (TCF).

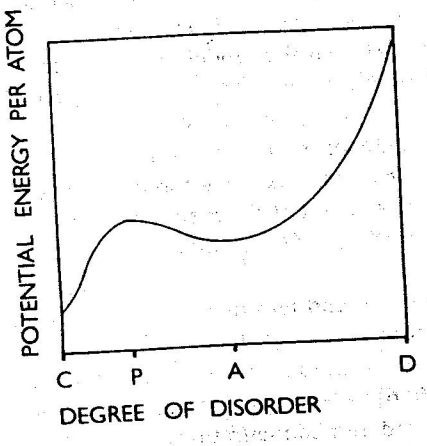

Fig. 1. Potential energy per atom of structures with an increasing degree of disorder. C — crystal, A — amorphous reproducible state, D — "totally" disordered state.

In this paper we want to emphasize the fact that for the correct estimation of the potential from the mentioned equations the entire TCF is not necessary [11], but only a certain kernel of the integral equation which is a function of two variables we must know (the TCF depends on three variables). Naturally, this kernel must be also approximated. This can be done in such a manner that the kernel is computed from the approximated TCF. Thus another aim of this paper is to check the validity of this approximation. In order to perform this, the computer model of glassy $Ni_{81}B_{19}$ is constructed and the simple method of calculation of this kernel from the model is derived. The statistical characteristics of the model are compared with the recently published experiments on this system and a quite good agreement is achieved. Then the kernel is computed from the model and also by using the superposition approximation for the TCF and the results are compared.

II. THEORY

Let us assume the M-component, homogeneous, isotropic, classical and equilibrium system of atoms, where the total potential energy is the sum of the pair

potentials. (Although metallic glasses are metastable systems in general, many of them have a very long relaxation time, so that the assumption of a stability in the room temperatures could be used). The volume and the absolute temperature of the system are V and T, respectively. Let us denote the pair central potential by $\varphi_{ab}(r)$, ϱ_c is the average number density, $g_{ab}(r)$ and $g_{abc}(r, t, s)$ are the pair and triplet correlation functions respectively, and the indexes a, b, c indicate the types of atoms. Then the second equation of the BBGKY hierarchy after some arrangements similar to those of Born and Green [9] could be presented in the form

$$U'_{ab}(r) = \varphi'_{ab}(r) + \sum_{1 \leqslant c \leqslant M} \int_0^\infty K_{abc}(s, r)\, \varphi'_{ac}(s)\, \mathrm{d}s \tag{1}$$

where

$$U_{ab}(r) = -k_B T \ln g_{ab}(r) \tag{2}$$

$$K_{abc}(s, r) = 4\pi s^2 \varrho_c \int_{|r-s|}^{r+s} \frac{t}{4r^2 s^2} (r^2 + s^2 - t^2)\, g_{abc}(r, t, s)\, \mathrm{d}t \tag{3}$$

and k_B is the Boltzmann constant. When $M > 1$, we obtain a system of integral equations ($a, b = 1, \ldots, M$). Because of a lack of information about the triplet correlations one has to use approximations. We used the superposition approximation [12], where the TCF is given by

$$g_{abc}(r, t, s) = g_{ab}(r)\, g_{bc}(t)\, g_{ca}(s). \tag{4}$$

Using (4) we find that the kernel given by (3) has the form

$$K_{abc}(s, r) = \frac{\pi}{r^2} \varrho_c g_{ca}(s) \int_{|r-s|}^{r+s} t(r^2 + s^2 - t^2)\, g_{cb}(t)\, \mathrm{d}t. \tag{5}$$

It is well known from the simulations of structure of some liquids that equation (4) is not correct at higher densities. This conclusion is also obvious from the recent molecular dynamics of the solid amorphous structure performed by Tanaka [13]. From the point of view of $\varphi'_{ab}(r)$ in equation (1) the complete knowledge of the TCF is not necessary [11]. For the correct estimation of the $\varphi'_{ab}(r)$ only the correctness of equation (5) is important. There is a possibility to check (5), because the kernel could be computed from the model exactly. The evaluation of the kernel from the model by definition (3) is somewhat inconvenient, so we proposed another way to calculate it. First some definitions are introduced. The conditioned TCF is defined by

$$g_{c/ba}(t, s/r) = g_{abc}(r, t, s)/g_{ab}(r). \tag{6}$$

Then we can define the conditioned PCF by

$$g_{c/ba}(s/r) = \frac{1}{2rs} \int_{|r-s|}^{r+s} t g_{c/ba}(t, s/r)\, dt = \tag{7}$$

$$= \int_0^{\pi} g_{c/ba}(\sqrt{r^2+s^2-2rs\cos\vartheta}, s/r) 2\pi s^2 \sin\vartheta\, d\vartheta$$

where the familiar equality $t^2 = r^2 + s^2 - 2rs\cos\vartheta$ was used. The next definition is the angular conditioned probability density

$$g^*_{c/ba}(\vartheta, s/r) = \frac{g_{c/ba}(\sqrt{r^2+s^2-2rs\cos\vartheta}, s/r)\sin\vartheta}{2g_{c/ba}(s/r)}. \tag{8}$$

Using these definitions it is possible to rewrite the kernel in the form

$$K_{abc}(s, r) = 4\pi\varrho_c s^2 g_{c/ba}(s/r)\, \overline{\cos\vartheta_{c/ba}(s/r)} \tag{9}$$

where

$$\overline{\cos\vartheta_{c/ba}(s/r)} = \int_0^{\pi} g^*_{c/ba}(\vartheta, s/r)\cos\vartheta\, d\vartheta. \tag{10}$$

The evaluation of the functions on the right-hand side of (9) from the model is relatively simple. Namely

$$g_{c/ba}(s/r) = \frac{1}{N_a 4\pi s^2 \varrho_c \Delta s} \sum_{i=1}^{N_a} \sum_{j=1}^{N_2(i)} \frac{N^{\ddagger}_3(i,j)}{N_2(i)}, \tag{11}$$

$$\overline{\cos\vartheta_{c/ba}(s/r)} = \frac{1}{N_a} \sum_{i=1}^{N_a} \sum_{j=1}^{N_2(i)} \sum_{\substack{k=1 \\ k\neq j}}^{N_3(i,j)} \frac{\cos\vartheta_{k/ij}}{N_2(i) N^{\ddagger}_3(i,j)} \tag{12}$$

and

$$N^{\ddagger}_3(i,j) = \begin{cases} N_3(i,j) - 1 & \text{when } s = r \text{ and } c = b \\ N_3(i,j) & \text{in all other cases} \end{cases} \tag{13}$$

where N_a is the number of atoms of the type a, $N_2(i)$ is the number of atoms of the type b for which $r - \Delta r/2 \leq d(i,j) < r + \Delta r/2$, $N_3(i,j)$ is the number of atoms of the type c for which $s - \Delta s/2 \leq d(i,k) < s + \Delta s/2$ and $d(l,m)$ denotes the distance between the atoms l, m. Further, $\cos\vartheta_{k/ij} = \bar{s}\,.\,\bar{r}/sr$ when assuming that the position of the atoms i, j, k are the same as in Fig. 2. In such a way we have avoided the evaluation of the TCF.

Model of glassy $Ni_{81}B_{19}$

The metallic glass $Ni_{81}B_{19}$ was chosen as a model system because of relatively precise experiments, from which the partial pair correlation functions are evaluated [14]. To begin with the coordinates of approximately 2000 atoms closed in a cube were created by the random number generator without any further restrictions.

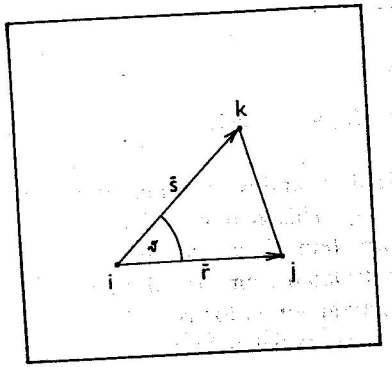

Fig. 2. Positions of atoms i, j, k for equation (12). Here $\cos\vartheta_{k/ij} = \bar{s}\,.\,\bar{r}/sr$, where $s = |\bar{s}|$ and $r = |\bar{r}|$.

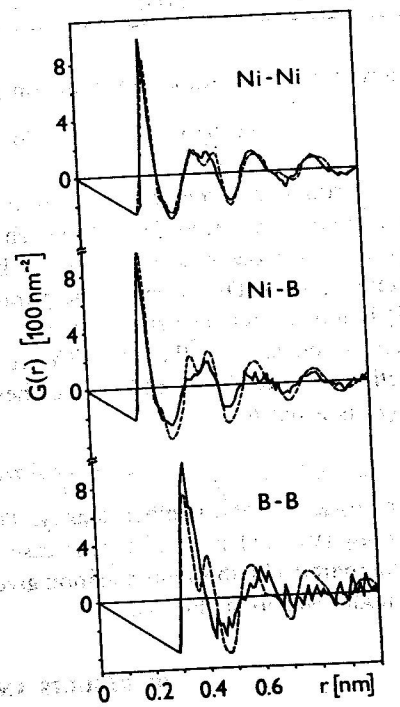

Fig. 3. A comparison of a model calculation (full curve) with experimental data of $Ni_{81}B_{19}$ [14] (broken curve) in the PRRDF.

The length of the edge of the cube was chosen in such a manner that the density was the same as the experimental one (8.4 g/cm³). The method of relaxation was the same as used by Kobayashi et al. [2]. The density was constant during the relaxation and periodical boundary conditions were used. The relaxation was stopped when the average displacement was about 0.0009 nm. Only negligible changes of the PCF were produced by further relaxation. The interactions are described by the truncated Morse potentials [3]

$$\varphi(r) = \begin{cases} D\{\exp[2\alpha(r_0 - r)] - 2\exp[\alpha(r_0 - r)]\} f\left(\frac{r - r_t}{r_0 - r_t}\right), & r \leq r_t \\ 0, & r > r_t \end{cases} \tag{14}$$

Table 1

Parameters of the Morse potentials used in the modelling of the metallic glass $Ni_{81}B_{19}$

Interaction	D [eV]	α [10 nm^{-1}]	r_0 [10^{-1} nm]	r_c [10^{-1} nm]
Ni—Ni	0.44891	1.8	2.64	3.6
Ni—B	0.4938	1.9	2.15	3.2
B—B	0.26935	1.8	3.4	4.3

where $f(z)$ is a modification function given by

$$f(z)=3z^4-8z^3+6z^2,\ z\leq 1;\ f(z)=1,\ z>1. \tag{15}$$

The parameters of the potentials are listed in Table 1, and were found intuitively after some trials (except D for Ni which is from [15]). This ineffective and heuristic approach is a consequence of the lack of information about the interaction in metallic glasses. Direct use of the parameters calculated from crystalline models [15] is not always successful, for example the parameter r_0 for Ni is 0.276 nm, which is too large in this case. The resulting partial radial reduced distribution functions (PRRDF) are in Fig. 3 together with the experimental ones. The PRRDF $G_{ab}(r)$ is given by

$$G_{ab}(r)=4\pi r\varrho_0(g_{ab}(r)-1) \tag{16}$$

where ϱ_0 is the total number density. Then the kernel (3) is computed from the model by (9), (11) and (12) for the case of a, b, c denoting Ni atoms. The results are compared with the approximation given by (5) where the partial Ni—Ni PCF of the model was used (Fig. 4).

III. RESULTS AND DISCUSSION

A good agreement with the experimental PRRDF in the case of the Ni—Ni correlation is obtained (Fig. 3), where the typical splitting of the second maximum is resolved. Tn the case of Ni—B and B—B correlations the agreement is not so good. The first peak of the Ni—B curve is nicely fitted, but the first submaximum of the second main maximum is weakly pronounced. Also a rather peculiar shape of the first main peak of the B—B curve is not produced. From these results it can be concluded that the interactions in the glassy $Ni_{81}B_{19}$ are not sufficiently approximated by the used potentials.

The calculated and approximated kernels for $r=0.25$; 0.32; 0.42; 0.55 [nm] are in Fig. 4. For the first maximum of the PCF ($r=0.25$ nm) the approximation is rather unsuccessful. For $r=0.32$ nm the dispersion of the kernel computed from the model is great because of a rare occurence of the pairs with the distance close to

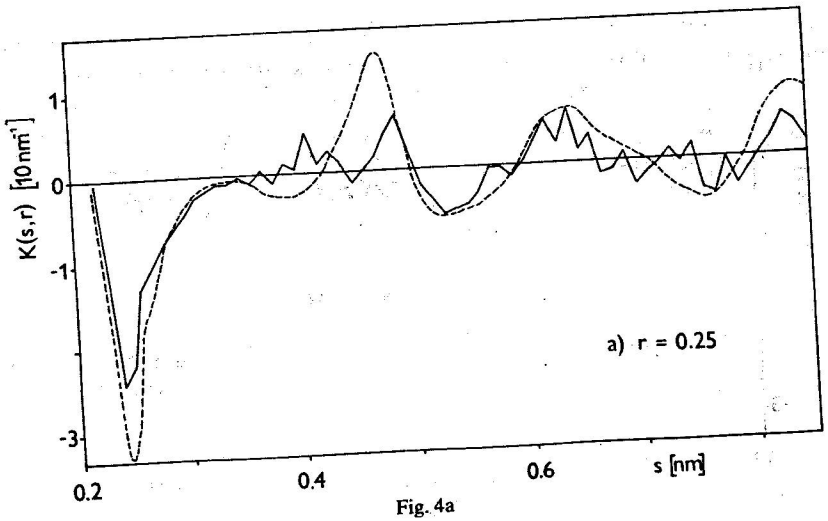

Fig. 4a

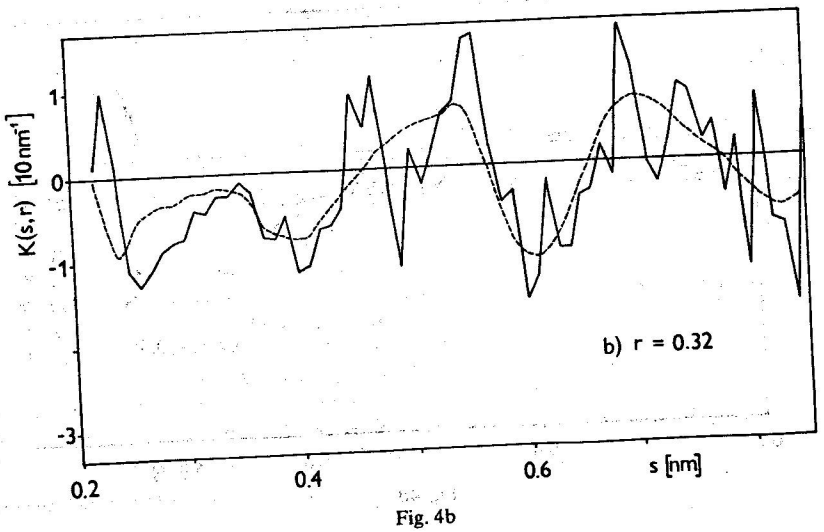

Fig. 4b

the first minimum of the PCF. Thus in that region of the variable r some further investigation must be performed. But for $r\geq 0.42$ nm it is obvious that the kernel is very well approximated by (5). This result is rather surprising when we take into account that in the amorphous system simulated by Tanaka [13] the TCF was approximated badly by (4) also for distances greater than the position of the first minimum of the PCF. The equation (3) rearranged into the integro-differential form with the approximation (4) (known as the Born-Green equation) was

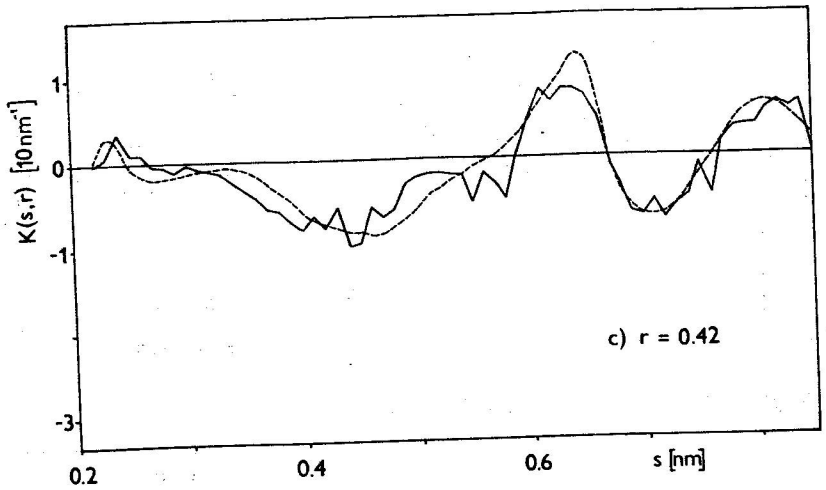

Fig. 4c

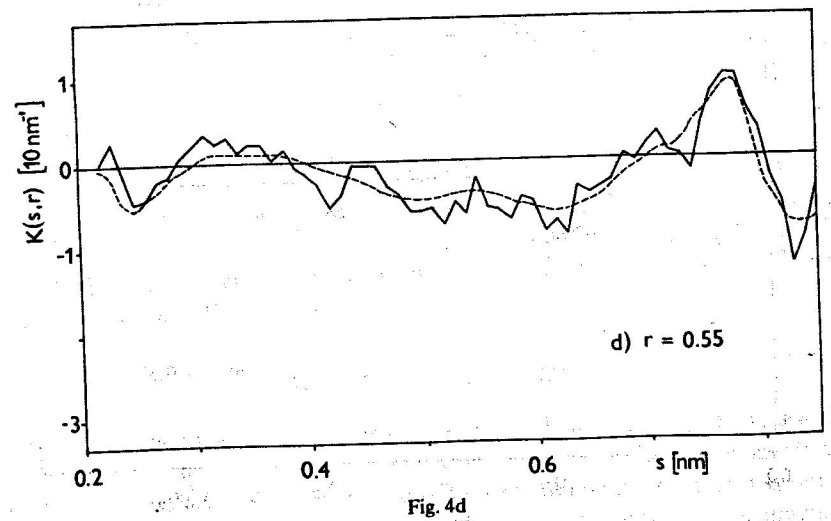

Fig. 4d

Fig. 4. The kernel of the integral equation (1) for Ni—Ni—Ni correlations: a) $r = 0.25$; b) $r = 0.32$; c) $r = 0.42$; d) $r = 0.55$ [nm]. Full curve: evaluation from the model by (9), (11), (12), broken curve: evaluation from the approximation (5).

frequently used for liquids and recently also for the solid amorphous system [16]. It is interesting that the conclusions are sometimes contradictory. For example Suda [17] concluded that the Born-Green equation without improvements is ill conditioned. On the other hand Fujiwara et al. [16] computed the potentials for the Cu—Zr amorphous system and problems were not reported. Although these discrepancies may be due to different methods of solution, the stability of equation (3) is the next problem to be investigated. To perform this a better approximation of the kernel (3) in the small r-region must be used. From this point of view the improvements of the superposition approximation found by Suda [17] seem to be promising.

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