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DIFFUSION IN RANDOM MIXED A-B ALLOYS IN THREE DIMENSIONS*

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Precision Monte Carlo simulations of labelled particle diffusion in random A-B alloys in three dimensions are reported. A variety of concentrations and ratios of the hopping rates $J^B/J^A = \eta$ are analysed. Results are compared with those predicted by available theories. The validity of these theories is observed to be strictly limited to region where $\eta > 1/z$ (z is the lattice coordination number).

1. Brief review of the theory

Manning[1] appears to have been the first to seriously address the problem of tracer diffusion in a random, multicomponent alloy. His analysis dealt with an important limiting situation where the vacancy concentration, v, is vanishingly small. Accordingly, if the constituent atom concentration for the species λ is c^λ, his work applies to the limit

$$v = (1 - \sum_\lambda c^\lambda) \to 0. \tag{1.1}$$

One of the traditional approaches to discussions of the tracer diffusion correlation factor, f_0, in single component alloys with vanishing vacancy concentration is to write[2]

$$f^0 = H/(H + 2J^0)_{v=0}. \tag{1.2}$$

* This work was done at Temple University computer center in Philadelphia, Pa., U. S. A.

Here J^0 is the hopping rate of the unique tracer and

$$H = JM, \tag{1.3a}$$

$$M = -(1 + \overline{\cos\Theta})/\overline{\cos\Theta}. \tag{1.3b}$$

The background particles have hopping rate J and $\overline{\cos\Theta}$ is the well known geometrical parameter of the lattice.

For the multicomponent alloy, Manning's work[1] amounts to introduce an ansatz for an effective single hopping parameter J^{eff}:

$$J^{eff} = \sum_{\lambda} (J^{\lambda} c^{\lambda} f^{\lambda})/\sum_{\lambda} (f^{\lambda} c^{\lambda}). \tag{1.4}$$

To make the analysis self-consistent, Eqs. (1.2) and (1.3) are rewritten in an »effective« form, i. e.,

$$f^0 = H^{eff}/(H^{eff} + 2J^0), \tag{1.5a}$$

where

$$H^{eff} = M J^{eff}. \tag{1.5b}$$

For an n-component alloy, Eqs. (1.5a) and (1.5b) constitute a set of $(n + 1)$ coupled equations for $(n + 1)$ unknowns, f^0 and f^{λ}. (Note, in this context Eq. (1.5a) can be rewritten as a set of n equations designating the tracer to be one of the background atoms of, say, species λ whereby, in Eq. (1.5a), $f^0 \to f^{\lambda}$ and $J^0 \to \to J^{\lambda}$. Similarly, if the tracer happens to be identical to one of the n-varieties of atoms in the background, the set of Eqs. (1.5a), (1.5b) has only n distinct members).

Although seemingly different, the viewpoint expressed above[3] is entirely equivalent to that of Manning[1]. Moreover, it has the advantage that it identifies the essence of the Manning ansatz in a form that lends itself to useful further generalization[4,5].

Manning's predictions were first tested in a detailed set of Monte Carlo simulations on bcc and fcc lattices by DeBruin et al.[3] who arrived at two important conclusions. First, they declared that: »The agreement between results by the simulation method and from Manning's calculations is excellent if the vacancy-atom exchange rates for the (two) components do not differ by much more than one order of magnitude«. Secondly, they stated that: »The Kikuchi-Sato[6] model, which was developed for ordered alloys, is not very successful for calculating correlation factors in random alloys. This is shown clearly by the considerable deviations over the entire frequency range and the incorrect values for self-diffusion correlation factors«.

In the present context, the above remarks may be interpreted as follows: For a two component alloy consisting of A and B atoms Manning's theory is reliable as long as the hopping rates are within the limits

$$J^B/J^A = \eta > \frac{1}{z}. \tag{1.6}$$

Here J^A and J^B are the hopping rates of the fast and the slow atoms, respectively. Note, any more precise conclusions than this, ought not to be drawn from the simulations reported in Ref. 3, where the sample sizes were in general relatively small (i. e., between $5 \times 5 \times 5$ and $19 \times 19 \times 19$) and the effective grand sample sizes not quite large enough (total vacancy jumps analyzed were approximately half a million).

Similar conclusions can again be drawn from a later Monte Carlo work on a simple cubic lattice by three of the same authors[7]. Here the effective sample sizes were similar and the lattice sizes were $13 \times 13 \times 13$ and $19 \times 19 \times 19$.

Despite this success, Manning's theory suffers from an important limitation that its applicability is restricted to the case of vanishing vacancy concentration. In view of the rapid changes in the dynamic characteristics of a tracer near the $v \to 0$ threshold[8], the $v \to 0$ theory cannot at all be applied even to the relatively small vacancy concentration limit of $v \cong 0.1$. (This contrasts strongly with the $(1 - v) = c \to 0$ limit results, which can often be applied, after simple meanfield like corrections, to the cases $c < 0.25$).

An attempt to extend the Manning theory to finite vacancy concentration has been made by Tahir-Kheli[4]. In this work, the representation of Manning's final expressions in the form given in Eqs. (1.4)—(1.5b) is exploited by analogy with the single component, $v \to 0$, Ref. 2 and its finite vacancy concentration extension achieved by Tahir-Kheli and Elliott[8] (henceforth to be referred to as TKE). The net result is that H^{eff} is transformed from its original form (1.5b) into the following:

$$H^{eff} = (M/(1 - v))\,(v\,J^0 f^0 + J^{eff}). \tag{1.7}$$

Clearly, for $v \to 0$ Eq. (1.6) reduces to Manning's result (1.5b). Similarly, for arbitrary v, but for a single component background, Eqs. (1.5a) and (1.6) together reduce to the TKE result (see Eq. (3.19) of Ref. 8).

As it is from the low vacancy limit, at the opposite concentration limit, i. e., for small particle concentrations (where $c^\lambda \ll 1$ for any λ and $\sum_\lambda c^\lambda = c \ll 1$) the above self-consistent theory is incorrect in the leading order c^λ (of course, it is exact when $c = 0$). On the other hand, for the intermediate concentrations, it can be expected to be moderately accurate for the diffusion correlation factor, especially that referring to the slow atoms. However, outside the range (1.6), this theory cannot be expected to provide accurate results. Such should especially be the case for the diffusion characteristics of the faster atoms. (For easy reference, henceforth, this theory will be referred to as TK1).

Another treatment, based on an extension of the TKE, but from the opposite limit of the concentration scale (namely, the small particle concentration $c \to 0$), also suffers from similar problems[5]. This theory (to be called TK2) is based on an equations of motion treatment whose truncations become increasingly inaccurate outside the range

$$z\,J^0 < J^{min}, \tag{1.8}$$

where J^{min} is the smallest hopping rate. For most physical systems that one ordinarily deals with, the specified range of hopping rates may be wide enough to be

useful. However, for situations where the hopping rates of the various components are vastly different, the TK2 cannot be expected to be satisfactory.

While the reader is best referred to the original[5] for details, it is convenient to give below the final results obtained in TK2. The tracer diffusion correlation factor f^0 in a mixed A-B system is given as follows:

$$f^0 = (1 + 2\,J^0\,\varrho_0/(M\,v_0))^{-1} \tag{1.9a}$$

where M is as defined in (1.3b) and

$$\varrho_0 = v\,J^0\,(c^A + c^B)\,J^B + c^B\,(1 - c^B)\,J^A - c^A\,c^B\,(J^A + J^B), \tag{1.9b}$$

$$v_0 = [v\,J^0 + (1 - c^B]\,J^A)\,[v\,J^0 + (1 - c^A)\,J^B] - c^A\,c^B\,J^A J^B. \tag{1.9c}$$

2. *Simulations and analysis of data*

Monte Carlo simulations in three dimensional minimally interacting systems have been described by many authors[9-11]. The new feature of the problem being discussed here is that systems with macroscopic concentrations of two different varieties of atoms are being treated. However, this feature is readily incorporated into the simulation routine.

Simulations were run for up to 500 MCS/P for $\eta = 1/\sqrt{2}$ and $c^A + c^B = c > 1/2$. For $\eta = 1/3$ and $c > 1/2$, they were run for 660 MCS/P. For $c < 1/2$, or $\eta = 1/10$, the runs were carried through to 1 000 MCS/P. Two different sets of network sizes were utilized. When the maximum MCS/P used was 660 or less, simple cubic networks of $20 \times 20 \times 20$, and $26 \times 26 \times 26$, sites each were used. For systems where the maximum time span was 1 000 MCS/P, the networks, were larger, i. e., $62 \times 26 \times 26$ and $30 \times 30 \times 30$.

Both large effective systems with ground sample (GS) of $N_G > 10^6$ particles each and the small systems (mini — GS sizes of $N_G \cong 70\,000$ atoms each) were used. The accuracy obtainable from the smaller systems is approximately 3—5 times worse. However, their results are, nevertheless, only of qualitative value.

The analysis

Monte Carlo simulations in three dimensional systems[9-11] have usually relied on achieving the »long time« limit. Therefore, the Einstein proportionality formula, relating the mean square displacement along a given axis to the diffusion coefficient D and the time elapsed τ, is used.

In practice, however, the relevant (MCS/P) time τ cannot be inordinary long. As a result, the standard Einstein formula needs to be supplemented with additional terms, i. e.,

$$\Delta_\lambda(\tau) = 2J^\lambda f^\lambda v^\lambda + const + O(J^\lambda \tau)^{-1}. \tag{2.1}$$

Here $\Delta_\lambda(\tau)$ is the mean square displacement after time τ of a particle of variety — λ measured along one of the three cartesian axes (for best statistics, Δ_λ is computed along all three axes and an average is then taken). The corresponding hopping rate (assumed to be spatially isotropic) is J^λ, v is the vacancy concentration and f^λ is the diffusion correlation factor of interest. Clearly, the unknown constant appearing in Eq. (2.1) is in itself of no particular importance. On the other hand, its absolute size is usually of order 0.1—1, and thus its neglect can cause errors of order 1% or so when the longest times used are of order 100—500. Accordingly, it is unwise to ignore the constant in Eq. (2.1).

Considering the long time behaviour, we choose an initial time τ_0, which is already long enough. (More will be said regarding this point later). For a time $\tau_1 > \tau_0$, write

$$L_\lambda(\tau_1 - \tau_0) = \Delta_\lambda(\tau_1) - \Delta_\lambda(\tau_0) = 2J^\lambda f^\lambda v(\tau_1 - \tau_0) + \\ + O(1/J^\lambda)(1/\tau_1 - 1/\tau_0).$$

Then look for the slope S_λ from the relationship

$$S_\lambda(\tau_1, \tau_0) = L_\lambda(\tau_1 - \tau_0)/(\tau_1 - \tau_0) + R. \tag{2.2}$$

It is clear that the remainder R on the right hand side of Eq. (2.2) is of order $(\tau_0\tau_1)^{-1}$. For large enough τ_0 and τ_1, this is obviously much smaller than the *const*, occuring in Eq. (2.1) and can therefore more safely be ignored.

Because S_λ is in general a function of both τ_0 and τ_1, it is best to take an average over the ensemble of such slopes that are obtained for all τ_0 and τ_1 so that the maximum value of τ_1 is at least 200 MCS/P smaller than the maximum length of the run. (This is to make sure that the last interval over which the slope is measured is at least 200 MCS/P wide). Both the average $\overline{S_\lambda}$ and its root mean square deviation δS are recorded. The diffusion correlation factor f_λ is now readily obtained from the relation

$$f = \overline{S_\lambda}/(2J^\lambda v). \tag{2.3}$$

The quantity $\delta S_\lambda/(2J^\lambda v) \equiv \delta_\lambda$ provides a workable measure of the inaccuracy to be expected. It is interesting that generally speaking δ_λ is also similar to the magnitude of the discrepancy between the two f^λ's computed from the »large« and the »small« network sizes mentioned earlier. Therefore, in what follows, we shall refer to δ_λ as being a meaningful estimate of the error in f^λ.

3. Results

For a simple cubic lattice, diffusion correlation factors, f^B and f^A, for a binary $A-B$ alloys with $\eta = 1/\sqrt{2}$, 1/3 and 1/10 are shown in Figs. 1, 2 and 3, respectively. These precision results were obtained from large GS's with $N_G > 10^6$ particles

each. For ready reference, the corresponding predictions of both the theories, TK1 and TK2 are also included. These simulations are expected to be accurate to within 2—6 parts per thousand.

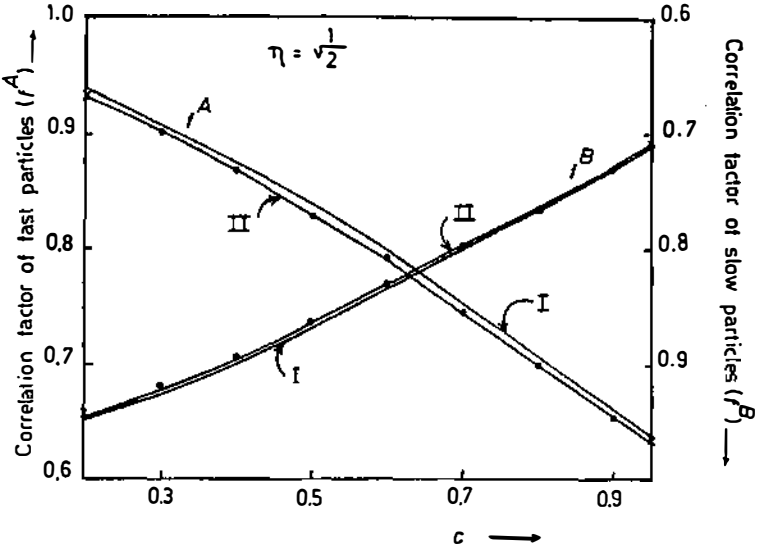

Fig. 1. The correlation factors f^A and f^B for the fast and the slow particles in simple cubic latice are plotted for $\eta = 1/\sqrt{2}$ as a function of the total concentration of A and B atoms, i. e., $c = c^A + c^B = 2c^A$. The continuous lines represent the theoretical results of theories TK1 and TK2 (indicated by indices I and II, respectivelly). The filled dark circles represent the precision simulation results given in Table 1. Similarly the crosses indicate the simulation estimates obtained from the smaller 70 000 particle samples.

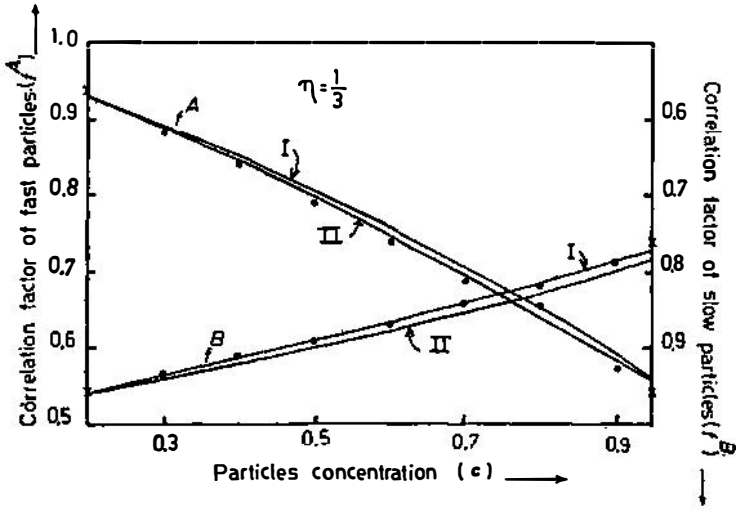

Fig. 2. Same as Fig. 1, except for η which is = 1/3.

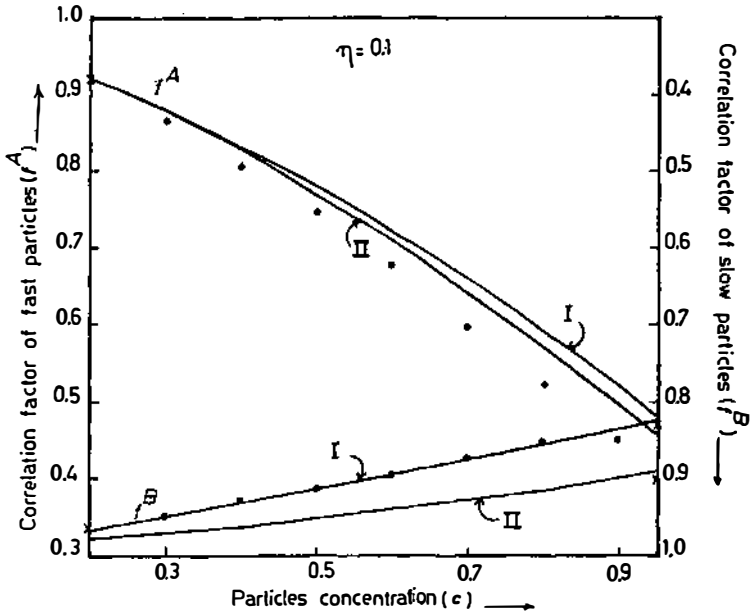

Fig. 3. Same as Fig. 1, except for η which is = 0.1.

TABLE 1.

c^A	f^A-precision simulation	f^B-precision simulation
0.475*	0.637* ± 0.010	0.716* ± 0.015
0.450	0.655 ± 0.003	0.727 ± 0.003
0.400	0.703 ± 0.003	0.758 ± 0.003
0.350	0.745 ± 0.003	0.796 ± 0.003
0.300	0.789 ± 0.004	0.827 ± 0.003
0.250	0.828 ± 0.004	0.860 ± 0.003
0.200	0.868 ± 0.004	0.891 ± 0.005
0.150	0.904 ± 0.006	0.916 ± 0.007
0.100*	0.929* ± 0.015	0.946* ± 0.015

Diffusion correlation factors, f^A and f^B, are listed for a three dimensional, simple cubic lattice for the case $c^A = c^B$ and $\eta = 1/\sqrt{2}$. These are the precision simulation results obtained from large GS's with effective particle numbers $N_G > 10^6$ each. The two starred samples (see the first column) are less accurate mini-GS's with 70 000 particles each.

4. *Discussion and concluding remarks*

It is clear from Figs. 1—5 that for the larger ratios η, i. e., for $\eta > 1/2$, both the theories, TK1 and TK2, are adequate. In particular, TK2 works well over the entire range of concentrations and its accuracy is roughly comparable to that of the simulation »experiment« itself.

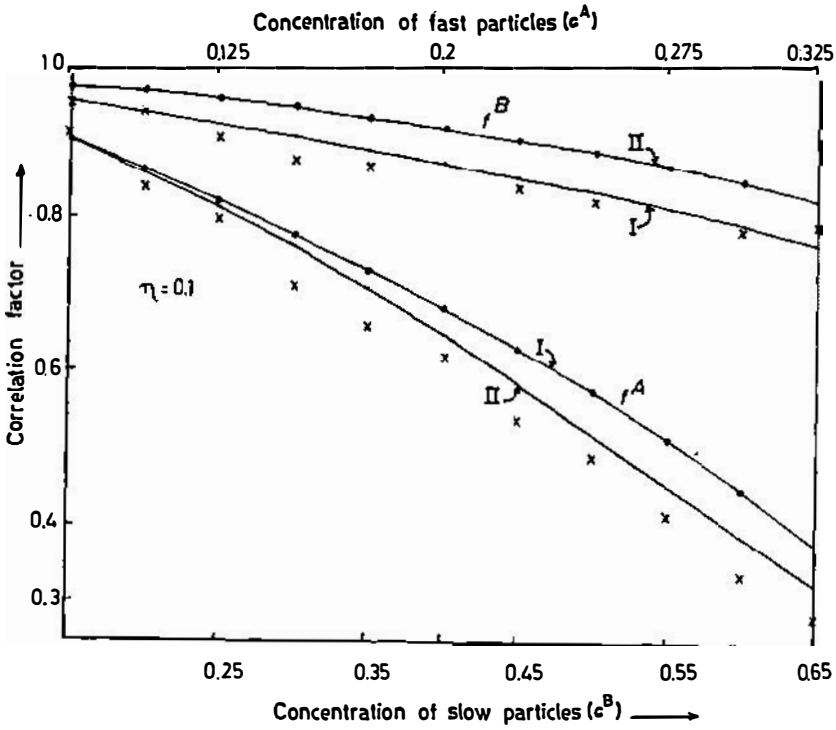

Fig. 4. For the simple cubic lattice correlation factors f^A and f^B are plotted as a function or c^A (or c^B). Here $\eta = 0.1$ and $c^A = 2c^B$.

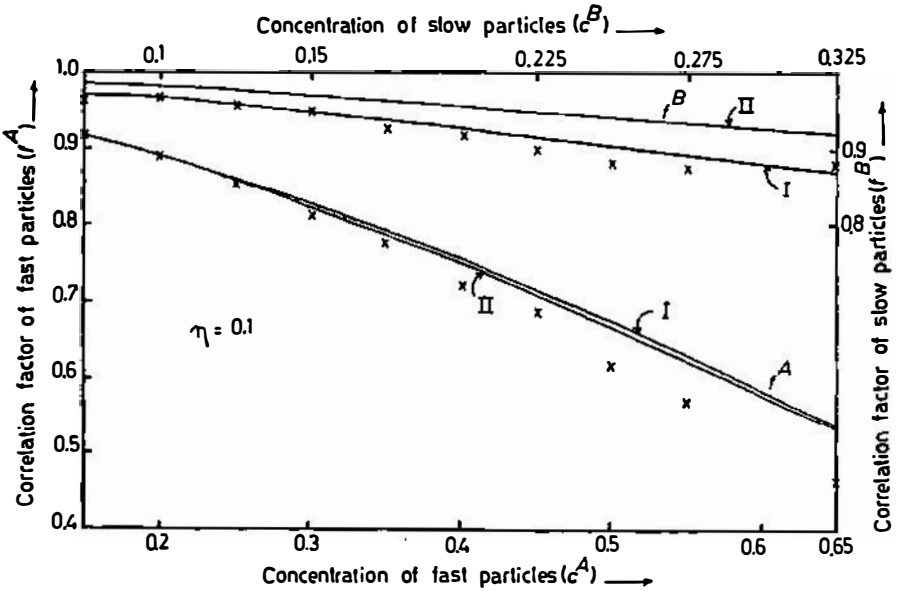

Fig. 5. Similar to Fig. 4 with difference that here $c^B = 2c^A$.

The self-consistent theory TK1, on the other hand, works satisfactorily only for the diffusion correlation factor relating to the slow atoms (which means, in the present case f^B). This feature of the theory though is not entirely unexpected. What is quite surprising, however, is the degree to which the TK1 predictions for f^A (namely, the correlation factor for the fast atoms) are in error. It is observed that even for $\eta = 1/3$, which is well within the range (1.6) the TK1 estimates for f^A are in error by 2—5% over a wide range of concentration. They are systematically too high. (see Figs. 1—5).

For $\eta = 1/10$, we are already outside the range where these theories are expected to be adequate. A look at Figs. 3—5 confirms this expectation, for $\eta = 0.1$ even TK2 is seen to be in error by approximately 3—10%. Qualitatively speaking, however, the predictions of TK2 are not unreasonable. Nevertheless, it is abundantly clear that the inequality (1.8) does indeed provide a realistic definition of the allowed range of hopping rates outside which the present theories have marginal applicability.

An interesting and unanticipated observation that emerges from these simulations is a new type of complementarity between the theories TK1 and TK2. What we mean here is that while on general grounds a certain complementarity between the two theories was indeed expected, it referred only to the concentration ranges: namely, that TK1 is a theory derived from the $v \to 0$ limit whereas TK2 is an outgrowth of the $c \ll 1$ decouplings. What has emerged, however, is different. TK2 is found to be better overall, including the intermediate concentration regime, but it is especially so for the diffusion characteristics of the fast atoms, i. e., for f^A. On the other hand, TK1, despite its intrinsic self-consistency, is inferior overall. Nevertheless, TK1 does moderately well for the *slow* atoms. With this empirical observation in hand, one can perhaps use TK1 and TK2 in combination to make predictions outside the range specified by the inequality (1.8).

To sum up, the existing theories[12-13] for the labelled particle diffusion in the mixed, random dynamic alloys in three dimensions are qualitatively useful within the range specified by the inequalities (1.6) and (1.8). Outside this range, the theories can only be used as empirical aid in interpreting the data. When this is done, TK1 should be used for the slow atoms and TK2 for the *fast* one.

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DIFUZIJA U NEUREĐENIM A-B LEGURAMA U TRI DIMENZIJE

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Prikazana je precizna Monte Carlo simulacija difuzije označenih čestica u neuređenim *A-B* legurama, u tri dimenzije. Ispitivan je niz slučajeva za različite koncentracije i omjere brzina preskoka $J^B/J^A = \eta$. Rezultati su uspoređeni s onima koje predviđaju postojeće teorije. Uočeno je, da je primjenljivost ovih teorija strogo ograničena na vrijednost parametra $\eta > 1/z$ (z je koordinacioni broj).