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## Calculation of the elastic energy of a solid solution

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### Abstract

A corrected version of the Microscopic Elasticity (ME) theory is proposed. Previous versions of this theory, like that of Khachaturyan, contained a discrepancy which caused severe problems in certain applications. One such case is the simulation of precipitation of secondary phases with long-ranged elastic interactions: Monte-Carlo simulations using the published ME theories to account for the elastic stresses profoundly fail to predict the precipitation of plate-like particles, like Guinier-Preston-Zones in Al-Cu-alloys. The quoted discrepancy is resolved, so that Monte-Carlo simulations using the new ME theory comply with all theoretical expectations. The revised theory also introduces new parameters such that real materials can be considered more accurately.

Keywords: microscopic elasticity theory; precipitation

### 1. Introduction

To perform a Monte Carlo (MC) simulation, a description of the energy of an atomic configuration is required. A very popular method is found in the use of a cluster expansion. An advantage of this approach remains its low computational cost for a simulation at the atomic scale. In a cluster expansion, the lattice positions are usually fixed such that they represent a perfect lattice. This rigid lattice is not adapted for the modelling of a lattice containing defects. But when modelling precipitation near a dislocation, for instance, a different approach should be considered. In a continuum medium, Hu and Chen [2] used the Macroscopic Elasticity theory of Khachaturyan to consider the dislocations' elastic stresses. At the atomic level, the Microscopic

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3 Elasticity (ME) theory of the same author [1] can be employed, according to current  
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5 understanding. But in MC simulations by the present authors using the ME theory as  
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7 defined by Khachaturyan, severe problems occurred.  
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10 In the quoted simulations, the precipitation of Guinier-Preston zones in AlCu  
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12 alloys was to be simulated. As an example, Guinier-Preston zones of type I are single  
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14 layers of Cu atoms in {100} planes. Their occurrence is known to be based on the  
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16 large size mismatch between Al and Cu atoms: this mismatch prevents the formation  
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18 of coherent voluminous particles because the corresponding elastic energy scales with  
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20 its volume, and is too high. In contrast, the formation of plate-like precipitates is not  
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22 prevented by elastic strains because these are similar to those of dislocations and  
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24 hence scale more favourably with length. But in the quoted MC simulations using  
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26 Khachaturyan's ME theory, always spherical precipitates emerged, even when the size  
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28 mismatch between Al and Cu atoms was greatly exaggerated. This is a strong  
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30 contradiction to both theoretical expectation and to well-known experimental  
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32 findings. The motivation for the present work was to find the cause for the  
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34 discrepancy. It lead to the development of a corrected version of the ME theory.  
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41 To assess the quality of the ME theory (starting with the original), the elastic  
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43 energies were also calculated in a more straightforward way for comparison. In this  
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45 approach, the energy changes in every time step of an MC simulation were derived  
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47 from a relaxation simulation of "atoms" interacting by harmonic potentials. The  
48  
49 relaxation was done using Molecular Statics (MS), i.e. a Molecular Dynamics [3]  
50  
51 program combined with a conjugate gradient algorithm [4] for the atomic relaxation.  
52  
53 When harmonic potentials are employed for the description of the atomic interactions,  
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55 the energy of a bond between two atoms of nature X and Y is given by:  
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$$V_{X-Y}(\Delta\mathbf{x}) = E_{X-Y} + \frac{\kappa_{X-Y}}{2} (\|\Delta\mathbf{x}\| - d_{X-Y})^2 \quad (1)$$

where  $E_{X-Y}$  represents the ground energy,  $\kappa_{X-Y}$  the bond stiffness, and  $d_{X-Y}$  the equilibrium length of the bond between atoms of type X any Y. The total energy of a configuration is then given by:

$$E^{(MS)} = \frac{1}{2} \sum_r \sum_{r' \neq r} \left( E_{n(r),n(r')} + \frac{\kappa_{n(r),n(r')}}{2} (\|r' - r\| - d_{n(r),n(r')})^2 \right) \quad (2)$$

where the field  $n(\mathbf{r})$  indicates the nature of the atom sitting at position  $\mathbf{r}$ . Compared to the application of the ME theory, the relaxation simulation and evaluation of equation (2) takes much more time to compute. But the MS method and its implementation are very simple and therefore virtually guaranteed to be free of programming or interpretation errors. Therefore this method is useful to assess ME theories (and implementations thereof).

The coupled MC-MS simulations of precipitation in AlCu alloys in fact yielded the formation of Guinier-Preston-zones of type I, in full agreement with both theoretical expectation and experimental findings. Therefore the ME theory has been revisited.

## 2. Derivation of the corrected ME theory

### 2.1 The binary solution case

The aim of the ME theory is to provide an evaluation of the change of stored elastic energy by a configuration change, like in Fig. 1 where the solute atom 13 exchanges its position with the matrix atom 9. This atomic move modifies the local elastic strains and consequently changes the amount of elastic energy stored in the lattice.

- insert fig. 1 about here -

To calculate the change of stored elastic energy, the transformation from I to II is decomposed in three steps (Fig. 2). In a first step, the atoms are repositioned from

1  
2  
3 their equilibrium positions (no stresses) to their positions in the reference lattice  
4 (symbolized by dashed lines in Fig. 2). The reference lattice corresponds to the  
5  
6 undistorted, periodic lattice, in which all atoms experience forces from their  
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8 neighbours. This step requires adding the energy  $\Delta E_{I \rightarrow I'}$  to the system. Then, the  
9  
10 solute atom 9 and the matrix atom 13 are exchanged in the reference lattice. This step  
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12 also modifies the energy of the system by a value  $\Delta E_{I' \rightarrow II'}$ . Finally, configuration II' is  
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14 relaxed to II, where the atoms reach their new equilibrium positions. This last step  
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16 reduces the energy of the system by  $\Delta E_{II' \rightarrow II}$ .  
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24 - insert fig. 2 about here -  
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28  
29 The first and the third steps are similar in nature: II'  $\rightarrow$  II corresponds to a  
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31 relaxation while I'  $\rightarrow$  I corresponds to the inverse of a relaxation. Hence, the energy  
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33 changes by these transformations are calculated the same way. When  $\mathbf{r}_{I'}$  represents the  
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35 atomic positions in configuration I', the positions in I can be described as  $\mathbf{r}_I + \mathbf{u}$ , where  
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37  $\mathbf{u}$  are the relaxation displacement vectors. Considering the harmonic approximation,  
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39 the energy of configuration I is evaluated by a first order Taylor expansion:  
40  
41  
42

$$43 \quad E(I) = E(I') - \mathbf{F}(I') \cdot \mathbf{u} + \frac{1}{2} (\mathbf{u}^T \cdot \mathbf{D} \cdot \mathbf{u}) \quad (3)$$

44  
45  
46 where  $\mathbf{F}(I')$  represents the net forces acting on the atoms in the reference lattice  
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48 positions and  $\mathbf{D}$  is the force constants matrix [6]. Since configuration I corresponds to  
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50 an equilibrium state, the displacements  $\mathbf{u}$  minimize equation (3), leading to  $\mathbf{F}(I') = \mathbf{D} \cdot \mathbf{u}$ .  
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53  
54 By introducing the Green tensor  $\mathbf{G}$  defined as  $\mathbf{G} = \mathbf{D}^{-1}$ , this can be transformed to  
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56  $\mathbf{u} = \mathbf{G} \cdot \mathbf{F}(I')$ , which in turn can be inserted for in equation (3) in order to eliminate the  
57  
58 unknown displacements. Then the transition energy  $(\Delta E)_{I' \rightarrow I}$  from configuration I' to I  
59  
60 can be expressed by the forces  $\mathbf{F}(I')$ :

$$(\Delta E)_{\Gamma \rightarrow \Gamma'} = E(\Gamma) - E(\Gamma') = -\frac{1}{2} \left( \mathbf{F}(\Gamma')^T \cdot \mathbf{G} \cdot \mathbf{F}(\Gamma') \right) \quad (4)$$

The determination of  $(\Delta E)_{\Gamma \rightarrow \Gamma'}$  is not straightforward. The dimension of the vector  $\mathbf{F}(\Gamma')$  is  $3N$  where  $N$  is the number of atoms contained in the configuration, making the size of the force constants matrix  $\mathbf{D}$  to be  $3N \times 3N$ . This large matrix size prevents from working in real space. But the determination of  $(\Delta E)_{\Gamma \rightarrow \Gamma'}$  becomes efficient in reciprocal space. The calculation is performed in the following for an alloy described by harmonic potentials. Using this description of the atomic interactions, only two parameters per bond type are necessary to evaluate the stored elastic energy of the configuration: the bond stiffness  $\kappa$  and the equilibrium length  $d$  of the bond. As the derivation of (4) in reciprocal space prevents from specifying different stiffness values (this aspect is discussed later on), all bonds are considered having the same stiffness  $\kappa$ .

The first step in the evaluation of  $(\Delta E)_{\Gamma \rightarrow \Gamma'}$  consists in determining the net force  $\mathbf{F}(\mathbf{r})$  felt by an atom located on the reference lattice  $\Gamma'$  at position  $\mathbf{r}$ . As already indicated, the atomic positions in this lattice correspond to the ones of the undistorted lattice without macroscopic stresses. When a solid solution is considered, this reference lattice has a lattice parameter  $a_{\text{ref}}$  which is a function of the solute concentration  $c_{\text{sol}}$ . A simple expression for  $a_{\text{ref}}$  valid for low solute concentrations reads

$$a_{\text{ref}} = (1 - c_{\text{sol}}) a_{\text{mat}} + c_{\text{sol}} a_{\text{sol}} \quad (5)$$

with  $a_{\text{mat}}$  and  $a_{\text{sol}}$  being the lattice parameters of the matrix and of a pure solute lattice, respectively. These lattice parameters are naturally linked to the equilibrium lengths of the pure element bond. In case of an fcc lattice,  $d = 2^{-1/2} a$ . By definition, the reference lattice is not in equilibrium: the force acting on some atoms is not zero. As

illustrated in Fig. 3, three different values of interatomic forces  $f$  may act on an atom in the reference lattice:

$$f_{\text{mat-mat}}(\mathbf{x}) = \kappa \left( 2^{-1/2} a_{\text{ref}} - d_{\text{mat-mat}} \right) \mathbf{x}^0 \quad (6)$$

$$f_{\text{mat-sol}}(\mathbf{x}) = \kappa \left( 2^{-1/2} a_{\text{ref}} - d_{\text{mat-sol}} \right) \mathbf{x}^0 \quad (7)$$

$$f_{\text{sol-sol}}(\mathbf{x}) = \kappa \left( 2^{-1/2} a_{\text{ref}} - d_{\text{sol-sol}} \right) \mathbf{x}^0 \quad (8)$$

Here,  $\mathbf{x}^0$  denotes the unit vector of  $\mathbf{x}$ . The net force  $\mathbf{F}(\mathbf{r})$  acting on an atom at position  $\mathbf{r}$  by all neighbours is dependent on the local configuration. When all atomic interactions are limited to the nearest neighbours like with harmonic potentials, four cases are possible:

(a) A matrix atom (No. 3 in Fig. 3-a) is only surrounded by matrix atoms. Each neighbouring matrix atom acts an interatomic force  $f_{\text{mat-mat}}$  on atom 3 (repulsive if  $d_{\text{mat-mat}} > 2^{-1/2} a_{\text{ref}}$  as in AlCu). But the sum of the interatomic forces, the net force  $\mathbf{F}$ , vanishes.

(b) A solute atom (Fig. 3-b) is only surrounded by matrix atoms. Atom 3 senses attractive interatomic forces  $f_{\text{mat-sol}}$  coming from the neighbouring matrix atoms. In such case, the net force felt by atom 3 also vanishes.

(c) A matrix atom (Fig. 3-c) has one solute atom as a neighbour (or several ones). Here the net force does not vanish but is  $f^{\text{net}} = f_{\text{mat-sol}} - f_{\text{mat-mat}}$ , because a matrix-matrix interaction is removed and a solute-matrix interaction is added compared to the case

(a).

(d) A solute atom (Fig. 3-d) has one solute atom as a neighbour (or several ones). This time, atom 3 experiences a net force  $f^{\text{net}} = f_{\text{sol-sol}} - f_{\text{sol-mat}}$  because a solute-matrix interaction is replaced by a solute-solute one compared to the case (b).

- insert fig. 3 about here -



An analytic expression for the net force  $\mathbf{F}(\mathbf{r})$  compatible with the four cases described above is required to work in reciprocal space. A useful formulation reads

$$\mathbf{F}(\mathbf{r}) = - \sum_{\mathbf{r}'} \mathbf{f}_{\text{mat-sol}}^{\text{net}}(\mathbf{r}-\mathbf{r}') \cdot c(\mathbf{r}') \cdot (1-c(\mathbf{r})) - \sum_{\mathbf{r}'} \mathbf{f}_{\text{sol-sol}}^{\text{net}}(\mathbf{r}-\mathbf{r}') \cdot c(\mathbf{r}') \cdot c(\mathbf{r}) \quad (9)$$

where  $\mathbf{f}_{\text{mat-sol}}^{\text{net}} = \mathbf{f}_{\text{sol-mat}} - \mathbf{f}_{\text{mat-mat}}$  and  $\mathbf{f}_{\text{sol-sol}}^{\text{net}} = \mathbf{f}_{\text{sol-sol}} - \mathbf{f}_{\text{sol-mat}}$  according to the cases (c) and (d), respectively, and  $c(\mathbf{r})$  represents the solute "concentration":  $c(\mathbf{r})=1$  if a solute atom is located at  $\mathbf{r}$ , and a matrix one if  $c(\mathbf{r})=0$ . In Khachaturyan's version of the ME theory, the net forces were wrongly accounted. In the expression of the relaxation energy  $\Delta F_6^{\text{relax}}$  in [1] (p. 451), they were expressed for the case of a binary phase as a sum over  $\mathbf{r}'$  of the term  $\mathbf{f}_{\text{Kanz.}}(\mathbf{r}-\mathbf{r}') \cdot c(\mathbf{r}')$ , where  $\mathbf{f}_{\text{Kanz.}}$  are the Kanzaki forces. This definition of the Kanzaki forces is incorrect because, as outlined above, they are not a function of  $(\mathbf{r}-\mathbf{r}')$  alone only but also of position  $\mathbf{r}$ , i.e., the nature of the target atom itself (atom 3 in Fig. 3). The Kanzaki forces accept two values in case of a binary solution, depending on the nature of the atom at  $\mathbf{r}$ :  $\mathbf{f}_{\text{Kanz.}} = \mathbf{f}_{\text{mat-sol}}^{\text{net}}$  when the atom at  $\mathbf{r}$  is a matrix atom, or  $(1-c(\mathbf{r}))=1$ , and  $\mathbf{f}_{\text{Kanz.}} = \mathbf{f}_{\text{sol-sol}}^{\text{net}}$  otherwise. The missing distinction of these two cases by  $c(\mathbf{r})$  in the definition of the Kanzaki forces explains the failure of the previous ME theory mentioned in the introduction. At a theoretical level, one may understand the origin of the error as a wrong definition of the stimuli in the Green's function analysis. When atoms showing a size misfit are considered, a stimulus actually corresponds to a small expansion or shrinking of an interatomic bond. But since a bond relates to two atoms, one has to count with care the stimuli. A simple spatial convolution involving the concentration field  $c(\mathbf{r})$  as in Khachaturyan's ME theory cannot achieve this task. This last statement is only valid at the atomic level. In the continuum, one can define a stimulus as the small expansion or shrinking

of a unit volume. Hence, the error only appears in the ME theory but not in the macroscopic theory of Khachatryan, which is widely used in phase field modelling for example.

The concentration field  $c(\mathbf{r})$  in real space has an image  $\hat{c}(\mathbf{k})$  in reciprocal space for a wave vector  $\mathbf{k}$  restricted to the first Brillouin zone [7]. The transformations from one space to the other are defined by

$$c(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{k}} \hat{c}(\mathbf{k}) \cdot e^{i\mathbf{k}\cdot\mathbf{r}} \quad (10)$$

and

$$\hat{c}(\mathbf{k}) = \sum_{\mathbf{r}} c(\mathbf{r}) \cdot e^{-i\mathbf{k}\cdot\mathbf{r}} \quad (11)$$

Using equation (9), the image of the net force in reciprocal space is

$$\begin{aligned} \hat{\mathbf{F}}(\mathbf{k}) = & - \sum_{\mathbf{r}} \left( \sum_{\mathbf{r}'} f_{\text{mat-sol}}^{\text{net}}(\mathbf{r}-\mathbf{r}') \cdot c(\mathbf{r}') \right) \cdot e^{-i\mathbf{k}\cdot\mathbf{r}} \\ & - \sum_{\mathbf{r}} \left( \sum_{\mathbf{r}'} (f_{\text{sol-sol}}^{\text{net}}(\mathbf{r}-\mathbf{r}') - f_{\text{mat-sol}}^{\text{net}}(\mathbf{r}-\mathbf{r}')) \cdot c(\mathbf{r}') \cdot c(\mathbf{r}) \right) \cdot e^{-i\mathbf{k}\cdot\mathbf{r}} \end{aligned} \quad (12)$$

The first term in equation (12) is easily derived because it represents a convolution in real space. Its expression in reciprocal space reads  $\hat{f}_{\text{mat-sol}}^{\text{net}}(\mathbf{k}) \cdot \hat{c}(\mathbf{k})$  [9] where

$\hat{f}_{\text{mat-sol}}^{\text{net}}(\mathbf{k})$  represents the image of  $f_{\text{mat-sol}}^{\text{net}}(\mathbf{r})$  in reciprocal space. On the other hand, the second term in (12) can't be analytically simplified in reciprocal space. But only elements where both  $c(\mathbf{r})$  and  $c(\mathbf{r}')$  don't vanish have to be accounted in the double sum over  $\mathbf{r}$  and  $\mathbf{r}'$ . These terms represent the bonding between two solute atoms. Since only few of such bonds exist in dilute alloys, the calculation of the second term of (12) is also in practice relatively simple and fast in real space.

Once  $\hat{\mathbf{F}}(\mathbf{k})$  is known, the lattice displacements  $\mathbf{u}$  are obtained in reciprocal space as  $\hat{\mathbf{u}}(\mathbf{k}) = \hat{G}(\mathbf{k}) \hat{\mathbf{F}}(\mathbf{k})$  where  $\hat{G}(\mathbf{k})$  is the image of the Green tensor in reciprocal

space. Finally, the change of elastic energy  $(\Delta E)_{X' \rightarrow X}$  from a stressed state  $X'$  in the reference lattice to the relaxed state  $X$  is given by

$$(\Delta E)_{X' \rightarrow X} = -\frac{1}{2N} \sum_{\mathbf{k}'} \left( \hat{F}_i(\mathbf{k}) \hat{G}_{ij}(\mathbf{k}) \hat{F}_j^*(\mathbf{k}) \right) \quad (13)$$

where  $i$  and  $j$  represent the axis coordinates and  $\hat{F}^*(\mathbf{k})$  is the conjugate of  $\hat{F}(\mathbf{k})$ .

Expression (13) allows the determinations of  $\Delta E_{I \rightarrow I'}$  and  $\Delta E_{II' \rightarrow II}$ .

The remaining quantity to evaluate is  $\Delta E_{I' \rightarrow II'}$ , the change of elastic energy when passing from configuration  $I'$  to  $II'$  in the reference lattice. This change is proportional to the changing number of solute-solute bonds. When the passage from  $I'$  to  $II'$  leads to the creation (or the annihilation) of  $M$  solute-solute bonds, the change of elastic energy from  $I'$  to  $II'$  equals

$$\Delta E_{I' \rightarrow II'} = M \cdot (E_{\text{mat-mat}}^{\text{ref}} + E_{\text{sol-sol}}^{\text{ref}} - 2E_{\text{mat-sol}}^{\text{ref}}) \quad (14)$$

where the  $E^{\text{ref}}$  quantities account for the elastic energy stored in the stretching of bonds to accommodate to the lattice parameter  $a_{\text{ref}}$  in the reference lattice. Their values are given for harmonic potentials as

$$E_{\text{mat-mat}}^{\text{ref}} = \frac{\mathbf{K}}{2} \left( 2^{-1/2} a_{\text{ref}} - d_{\text{mat-mat}} \right)^2 \quad (15)$$

$$E_{\text{mat-sol}}^{\text{ref}} = \frac{\mathbf{K}}{2} \left( 2^{-1/2} a_{\text{ref}} - d_{\text{mat-sol}} \right)^2 \quad (16)$$

$$E_{\text{sol-sol}}^{\text{ref}} = \frac{\mathbf{K}}{2} \left( 2^{-1/2} a_{\text{ref}} - d_{\text{sol-sol}} \right)^2 \quad (17)$$

In another ME theory proposed by Cook and de Fontaine [5], the elastic energy change  $\Delta E_{I' \rightarrow II'}$  of equations (14) to (17) was accounted. This helped to obtain a better agreement with MS relaxations, as is shown later on, but otherwise this theory contained the same error as the more widely known one from Khachatryan.

## 2.2 Extension to multicomponent alloys

Like the previous theory developed by Khachaturyan [1], the corrected ME theory can be extended to multicomponent alloys. The central point in this extension is the definition of an expression of the net force  $\mathbf{F}(\mathbf{r})$  acting on position  $\mathbf{r}$  of the reference lattice.

When the system is composed of solute elements of  $n$  different natures,  $n$  concentration fields are defined as  $c_p(\mathbf{r})=1$  if the atomic position at  $\mathbf{r}$  is occupied by a solute atom of nature  $p$  ( $1 \leq p \leq n$ ), and  $c_p(\mathbf{r})=0$  otherwise. Using this convention, a matrix atom is located at  $\mathbf{r}$  when

$$\sum_{p=1}^n c_p(\mathbf{r}) = 0 \quad (18)$$

The net force applied on this matrix atom surrounded by solute atoms of different nature is then defined as:

$$\mathbf{F}_0(\mathbf{r}) = - \sum_{p=1}^n \sum_{\mathbf{r}'} (\mathbf{f}_{p0}(\mathbf{r}-\mathbf{r}') - \mathbf{f}_{00}(\mathbf{r}-\mathbf{r}')) \cdot c_p(\mathbf{r}') \cdot \left( 1 - \sum_{q=1}^n c_q(\mathbf{r}') \right) \quad (19)$$

where  $\mathbf{f}_{p0}$  indicates the interatomic force between a solute atom of nature  $p$  and a matrix atom of nature 0, by convention. In case of a solute atom only surrounded by matrix atoms, the net force  $\mathbf{F}(\mathbf{r})$  applied on it vanishes. When a solute of nature  $q$  is surrounded by other solute atoms, it experiences the net force

$$\mathbf{F}_q(\mathbf{r}) = - \sum_{p=1}^n \sum_{\mathbf{r}'} (\mathbf{f}_{pq}(\mathbf{r}-\mathbf{r}') - \mathbf{f}_{q0}(\mathbf{r}-\mathbf{r}')) \cdot c_p(\mathbf{r}') \quad (20)$$

where  $\mathbf{f}_{pq}$  represents the interatomic force between a solute atom of nature  $p$  and another atom of nature  $q$ . All the interatomic forces are defined in an fcc lattice with lattice parameter  $a_{\text{ref}}$  as:

$$\mathbf{f}_{pq}(\mathbf{r}) = \kappa \left( 2^{-1/2} a_{\text{ref}} - d_{pq} \right) \mathbf{r}^0 \quad (21)$$

where  $d_{pq}$  represents the equilibrium bond length between atoms of natures  $p$  and  $q$ .

Uniting all the cases into a single expression for  $F(\mathbf{r})$ , one obtains from equations (19)

and (20):

$$\begin{aligned}
 F(\mathbf{r}) = & - \sum_{p=1}^n \sum_{\mathbf{r}'} (f_{p0}(\mathbf{r}-\mathbf{r}') - f_{00}(\mathbf{r}-\mathbf{r}')) \cdot c_p(\mathbf{r}') \\
 & - \sum_{q=1}^n \sum_{p=1}^n \sum_{\mathbf{r}'} (f_{pq}(\mathbf{r}-\mathbf{r}') + f_{00}(\mathbf{r}-\mathbf{r}') - f_{q0}(\mathbf{r}-\mathbf{r}') - f_{p0}(\mathbf{r}-\mathbf{r}')) \cdot c_p(\mathbf{r}') c_q(\mathbf{r})
 \end{aligned} \tag{22}$$

Once the expression  $F(\mathbf{r})$  is known, the same method as in the binary solution case can be applied to determine the relaxation energies  $\Delta E_{I \rightarrow I'}$  and  $\Delta E_{II' \rightarrow II}$ . The third energy term  $\Delta E_{I' \rightarrow II'}$  corresponding to the change of stored elastic energy in the reference lattice is evaluated in a similar manner as in the binary case:

$$\Delta E_{I' \rightarrow II'} = \sum_{p=1}^n \sum_{q=1}^n M_{pq} \cdot (E_{pq}^{\text{ref}} + E_{00}^{\text{ref}} - E_{p0}^{\text{ref}} - E_{q0}^{\text{ref}}) \tag{23}$$

where  $M_{pq}$  represents the number of bond changes between atoms of natures  $p$  and  $q$  during the transformation from configuration I' to II'. The unit energies  $E_{pq}^{\text{ref}}$  are defined as:

$$E_{pq}^{\text{ref}} = \frac{\kappa}{2} \left( 2^{-1/2} a_{\text{ref}} - d_{pq} \right)^2 \tag{24}$$

### 3. Accuracy of the calculation

The assessment of the accuracy of the ME theory is performed by comparing the results achieved with the ME theory with those obtained using MS relaxations. When the same harmonic potentials are used as input, the agreement should be perfect. In the calculations below, harmonic potentials were employed with the parameters:  $d_{\text{mat-mat}}=2.85\text{\AA}$ ,  $d_{\text{sol-sol}}=d_{\text{mat-sol}}=2.56\text{\AA}$ , and  $\kappa_{\text{mat-mat}}=\kappa_{\text{mat-sol}}=\kappa_{\text{sol-sol}}=1.4 \text{ eV/\AA}^2$ .

A first consistency test was conducted by looking at the energy of a configuration containing only two solute atoms as a function of the distance between

1  
2  
3 the two solute atoms expressed in the number of neighbour shells NN (Fig. 4). There  
4 is a perfect agreement between MS relaxations and all ME theories when  $NN > 1$   
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6 (errors below 1meV). The situation is however different for the first neighbour shell,  
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8 where the ME theory of Khachatryan provides a value 30meV lower than the  
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10 configuration energy obtained with MS relaxations. For the ME theory of Cook and  
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12 de Fontaine [5] as well as the present one, the agreement remains excellent even for  
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NN=1.

A second test consists in adding one more solute atom. Starting from a  
configuration where two solute atoms in positions  $r_1$  and  $r_2$  are first nearest  
neighbours, the third solute atom is introduced at different locations  $r_3$ . Depending on  
the position of the third atom, the configuration energy is dependent on two  
quantities: the distance in neighbour shells NN between  $r_3$  and  $r_1$ , and the angle  $(r_2 - r_1, r_3 - r_1)$ . The calculations with three atoms (Tab. 1) show that only the new version of  
the ME theory provides a correct estimation ( $\pm 3\text{meV}$ ) of the configuration energies  
derived by MS relaxations. The Cook-de Fontaine version fails for one case, and the  
Khachatryan version in several configurations.

- insert fig. 4 and tab. 1 about here -

The most striking difference between the previous ME theories and the  
version presented here is the capacity of the latter to simulate the correct shape of GP  
zones in AlCu alloys. As mentioned in the introduction, only spherical precipitates  
were obtained by MC simulations using the previous theories (both of them). On the  
other hand, plates located in  $\{100\}$  lattice planes (Fig. 5) as observed experimentally

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3 in AlCu alloys nucleate during an MC simulation with the new ME theory. Details on  
4 this phenomenon are discussed in [10].  
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8 It should be noted that for certain kinds of physical mechanisms, the  
9 distinction between the various theories can be unimportant. Simulations of solute  
10 atom diffusion may be an example for this, when the solutes get in direct contact only  
11 rarely anyway. But in the present case of precipitation, where solute atoms tend to  
12 group and form nuclei for particles, it is particularly important to calculate the  
13 configuration energies of the nuclei correctly.  
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#### 29 **4. Towards modeling of a real material**

30 An additional improvement provided by the corrected ME theory is its ability to  
31 model more cases than before. In previous theories, only one misfit information could  
32 be managed: the matrix-solute bond always had the same equilibrium length as the  
33 solute-solute bond. In contrast, the new version differentiates the equilibrium length  
34 of the matrix-solute interaction from the solute-solute one. This new degree of  
35 freedom helps driving important conclusions on the effects of elastic strains on  
36 precipitation, as is shown in [10].  
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47 Meanwhile, the derived ME theory still possesses a serious inconvenience: all  
48 bonds have the same stiffness. The reason for this limitation relates to the definition  
49 of the force constants matrix. When atoms of two different types are present in the  
50 lattice, the large matrix  $D$  can be expressed as a combination of small local force  
51 constant matrices of size  $3 \times 3$  like the following ones for the [110] first neighbour  
52 interaction in fcc an lattice:  
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$$\mathbf{D}_{X-Y}^{\text{loc}} = \frac{1}{2} \begin{pmatrix} \kappa_{X-Y} & \kappa_{X-Y} & 0 \\ \kappa_{X-Y} & \kappa_{X-Y} & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (25)$$

where X-Y represents any combination mat-mat, mat-sol or sol-sol. Using these local force constants matrixes, the net force acting on an atom at  $\mathbf{r}$  can be expressed by

$$\mathbf{F}(\mathbf{r}) = \sum_{\mathbf{r}'} \mathbf{D}_{n(\mathbf{r}),n(\mathbf{r}')}^{\text{loc}} (\mathbf{r} - \mathbf{r}') \cdot \mathbf{u}(\mathbf{r}') \quad (26)$$

where  $n(\mathbf{r})$  indicates the type of the atom at  $\mathbf{r}$ . Since a unique small local force constants matrix does not exist, the convolution over  $\mathbf{r}'$  can't be simplified in reciprocal space and, hence, there is no valid formulation like  $\hat{\mathbf{F}}(\mathbf{k}) = \hat{\mathbf{D}}(\mathbf{k}) \cdot \hat{\mathbf{u}}(\mathbf{k})$  with a small 3×3 matrix  $\hat{\mathbf{D}}(\mathbf{k})$  which could be afterward easily inverted to obtain a simple 3×3 Green tensor in reciprocal space. However, a difference in bond stiffness can be roughly accommodated by the following consideration. When different stiffness values are considered, the interatomic force  $f_{\text{mat-sol}}$  defined by equation (7) is multiplied by the factor  $(\kappa_{\text{mat-sol}}/\kappa_{\text{mat-mat}})$ . But, at the same time, the local force constants matrix is also locally multiplied by the same factor. Hence a stronger net force exists in a stiffer matrix when  $\kappa_{\text{mat-sol}} > \kappa_{\text{mat-mat}}$ . In such a situation, one can assume that the lattice displacements during the relaxation will be of the same amplitude. Consequently, the relaxation energy determined by equation (13) is only multiplied by a factor  $(\kappa_{\text{mat-sol}}/\kappa_{\text{mat-mat}})$ . A simple transformation which leads to this result and remains inexpensive to implement in the relaxation energy calculation consists in the multiplication of the interatomic forces by a suitable square root, i.e. equation (27) may be used instead of (21):

$$f_{pq}(\mathbf{r}) = \sqrt{\kappa_{pq} \kappa_{00}} \left( 2^{-1/2} a_{\text{ref}} - d_{pq} \right) \mathbf{r}^0 \quad (27)$$



The change of bond stiffness also modifies the expression of the bond energies  $E^{\text{ref}}$  in the reference lattice, where the specific stiffness has to be considered instead of a general  $\kappa$  value in expressions (15) to (17).

Performing the modifications of the model described above, the consideration of different bond stiffness is illustrated in an AlCu model alloy with stiffness  $\kappa_{\text{AlAl}}=1.4\text{eV}/\text{\AA}^2$  (giving the elastic constants  $C_{11}^{\text{Al}}=112\text{GPa}$  and  $C_{12}^{\text{Al}}=C_{44}^{\text{Al}}=56\text{GPa}$ ) and  $\kappa_{\text{CuCu}}=2.1\text{eV}/\text{\AA}^2$  ( $C_{11}^{\text{Cu}}=187\text{GPa}$  and  $C_{12}^{\text{Cu}}=C_{44}^{\text{Cu}}=93\text{GPa}$ ). As before, the straightforward MC-MS simulation is used as a benchmark. The results (Tab. 2) for a configuration with two solute atoms and for different Al-Cu bond stiffness  $\kappa_{\text{AlCu}}$  indicate that the method described by equation (27) qualitatively reproduces the influence of a difference of bond stiffness. However, discrepancies of the order of 0.01eV are observed for the first nearest neighbour interaction.

- insert tab. 2 about here -

Until now, it has also been assumed that the nature of the atomic interactions is purely harmonic. Such description of the bonding between atoms only allows the modelling of a material with a specific relation between elastic constants  $C_{12}=C_{44}=C_{11}/2$ , which induces a specific anisotropy ratio  $\chi=(C_{11}-C_{12})/(2C_{44})$  of 0.5. In order to model a material with a different anisotropy ratio, the description of the force constants matrix should be modified. This can be also done, as shown in [10].

## 5. Conclusion

A new Microscopic Elasticity theory has been derived and validated by using slow, but unequivocal Molecular Statics simulations. The new version corrects a discrepancy found in earlier versions. Unlike the latter, the application of the present

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3 version in Monte-Carlo simulations of precipitation yields results that are in full  
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5 agreement with theoretical expectations and with experimental findings in Al-Cu  
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7 alloys. Moreover, the new version puts an emphasis on the atomic bonds instead of  
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9 just differing atom sizes. This introduces new, independent elastic parameters  
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11 (distinction between solute-solute bonds and solute-matrix ones) and thereby widens  
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13 the scope in which linear elasticity can be used to describe and understand atomic  
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15 behaviour.  
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### 21 **Acknowledgements**

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23 Research program of the Netherlands Institute for Metals Research in the Netherlands (www.nimr.nl).  
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### 53 **Figure captions**

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55 Figure 1. Configuration change due to an exchange of position between a solute and a  
56 matrix atom  
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59 Figure 2. Decomposition of the transformation in three steps  
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Figure 3. Net force acting on an atom in the reference lattice

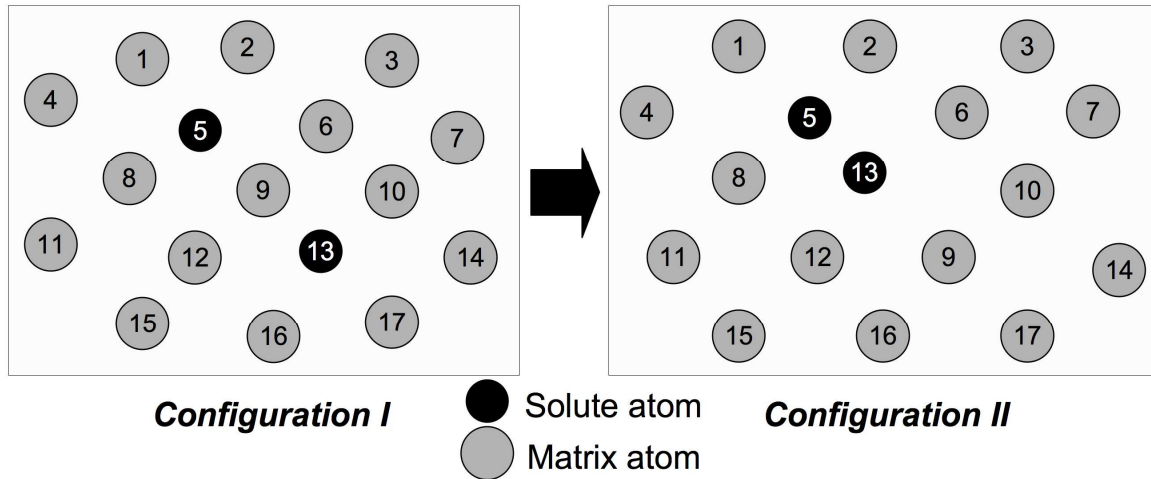
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8 the new ME theory. only Cu-atoms are displayed.  
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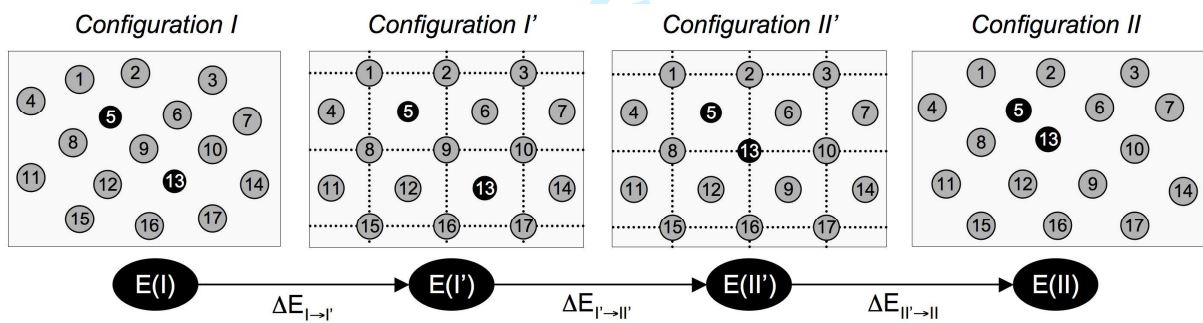
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18 Table 2. Consideration of different bond stiffness: configuration energies with two  
19 solute atoms using the ME theory and MS relaxations  
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**Figure 1.** Configuration change due to an exchange of position between a solute and a matrix atom



**Figure 2.** Decomposition of the transformation in three steps

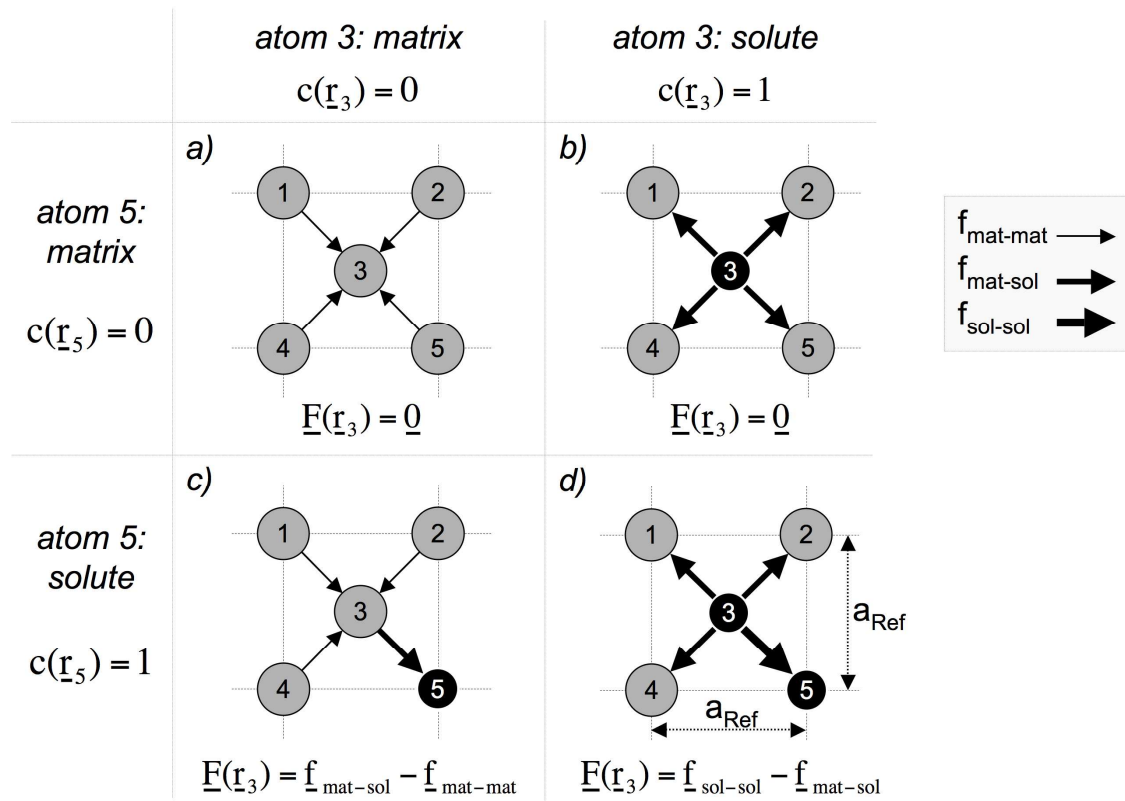


Figure 3. Net force acting on an atom in the reference lattice

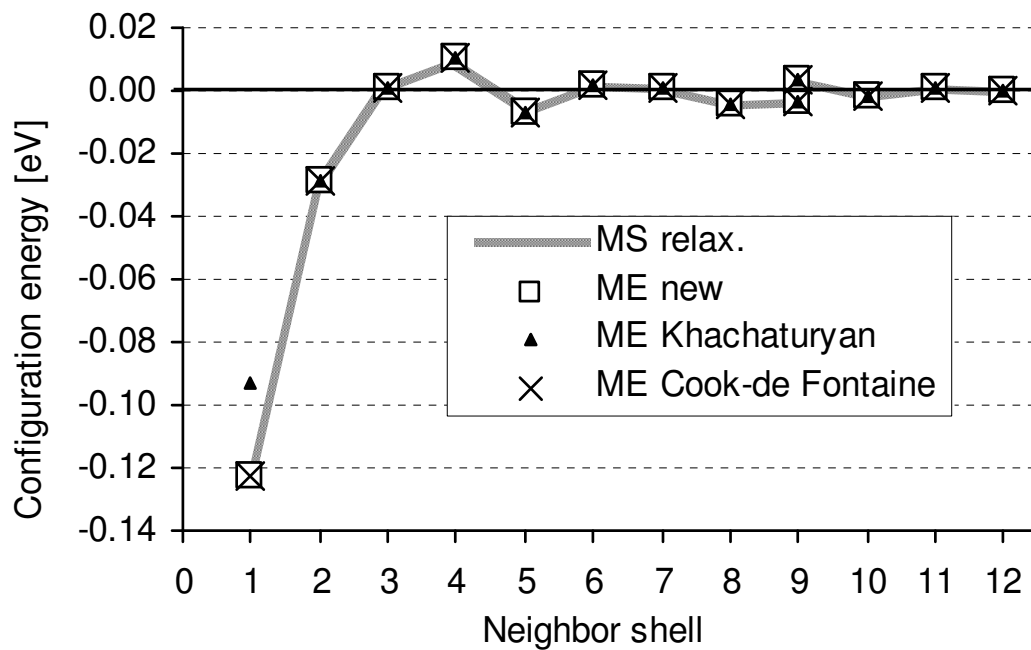
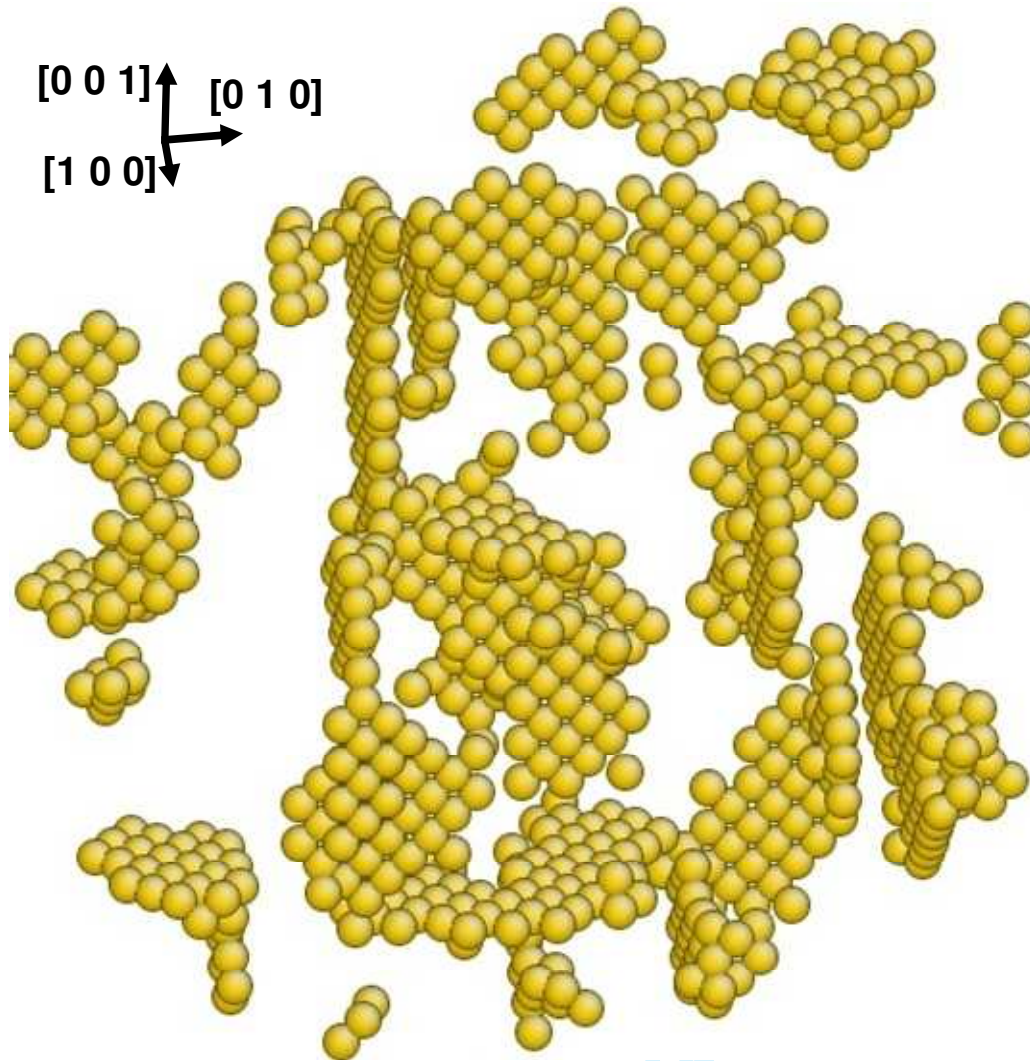


Figure 4. Configuration energies with two atoms



**Figure 5.** Atomic configuration from an MC simulation in an Al3%at.Cu alloy using the new ME theory. only Cu-atoms are displayed.

NN	Angle	MS relax. [eV]	Error ME theory [eV]		
			new	Khacha.	C.-de F.
<b>1</b>	60°	-0.188	0.000	<b>0.030</b>	<b>-0.026</b>
	90°	-0.146	-0.002	<b>0.027</b>	-0.001
	120°	-0.123	0.000	<b>0.026</b>	-0.002
	180°	-0.128	0.000	<b>0.029</b>	0.001
<b>2</b>	45°	-0.146	-0.002	<b>0.027</b>	-0.001
	90°	-0.020	-0.001	-0.001	-0.001
	135°	-0.033	0.000	0.000	0.000
<b>3</b>	30°	-0.123	0.000	<b>0.026</b>	-0.002
	55°	-0.020	-0.001	-0.001	-0.001
	73°	0.006	0.000	0.000	0.000
	90°	0.016	0.001	0.001	0.001
	107°	-0.006	0.001	0.001	0.001
	125°	0.002	0.001	0.001	0.001
	150°	0.000	0.001	0.001	0.001

**Table 1.** Configuration energies with three atoms

NN	$\beta_{\text{AlCu}} = 1.4 \text{ eV/\AA}^2$		$\beta_{\text{AlCu}} = 1.7 \text{ eV/\AA}^2$		$\beta_{\text{AlCu}} = 2.1 \text{ eV/\AA}^2$	
	MS relax. [eV]	Error ME th. [eV]	MS relax. [eV]	Error ME th. [eV]	MS relax. [eV]	Error ME th. [eV]
<b>1</b>	-0.066	0.005	-0.126	-0.006	-0.185	-0.025
<b>2</b>	-0.028	0.000	-0.042	-0.001	-0.057	-0.003
<b>3</b>	0.001	0.001	0.003	0.000	0.005	-0.001
<b>4</b>	0.010	0.001	0.017	-0.001	0.026	-0.003
<b>5</b>	-0.007	0.001	-0.011	0.001	-0.015	0.001
<b>6</b>	0.001	0.001	0.002	0.001	0.004	0.001
<b>7</b>	0.001	0.001	0.002	0.001	0.003	0.001
<b>8</b>	-0.004	0.001	-0.006	0.001	-0.009	0.001

**Table 2.** Consideration of different bond stiffness: configuration energies with two solute atoms using the ME theory and MS relaxations