Eur. Phys. J. B **45**, 419–424 (2005)
DOI: 10.1140/epjb/e2005-00199-x

THE EUROPEAN PHYSICAL JOURNAL B

Structure of grain boundaries in nanostructured powders: a Monte-Carlo/EAM numerical investigation

M. Grafouté, Y. Labaye, F. Calvayrac, and J.M. Grenèche[a]

Laboratoire de Physique de l'État Condensé, UMR CNRS 6087, Université du Maine, 72085 Le Mans Cedex 9, France

Received 4 February 2005
Published online 6 July 2005 –

Abstract. A new approach based on the Embedded Atom Method is applied to model the structure of grain boundaries in nanostructured powders. We choose a set of EAM parameters reproducing bcc as well as fcc structures. A Monte-Carlo scheme, namely various modifications of the well established simulated annealing/Metropolis algorithm, is used to obtain realistic structures of twisted and tilted double and triple grain boundaries as a function of the relative disorientation of the grains. We devise a completely general way to take into account the structure of the grains far from the interface as well as to constraint the relative orientation of the grains, without using periodic boundaries conditions, which would restrict the simulation to certain relative twist or tilt angles for the grains. A few parameters having to be assumed, we compare two methods to model the structure of the grain boundaries. As these two methods, depending on different parameters, lead to similar results, we therefore reduce the number of parameters to be assumed. Results indicate a new configuration which is closer to the bcc structure than the fcc one in the case of iron nanopowders.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 05.10.Ln Monte Carlo methods – 61.72.Mn Grain and twin boundaries

1 Introduction

The solid-state processing technique of high energy ball milling involves successive fragmentation and welding stages of a microcrystalline powder into a random assembly of nanocrystalline grains, giving rise to the so-called nanostructured materials [1]. This non-equilibrium state is obviously not the lowest energy one as it would be a quasi-infinite perfectly crystalline bulk at room temperature and pressure. In those conditions, however, the nanostructured state is metastable on macroscopic time scales. The simulation of the milling process thus has to address very different time and length scales: mechanical shocks between either particles or particles and ball or vials take place at about a millisecond time scale, while the reorganization of the crystalline structures occurs on a picosecond time scale. Direct molecular dynamics simulation can be thus ruled out to model the atomic microstructure.

Similar problems arise about the size of the systems: they present disordered interfaces or grain boundaries on a nanometer scale (up to 20 nm), when the grains themselves can be almost crystalline on a much larger scale. The atomic fraction localised in those grain boundaries which is dependent on the conditions of synthesis, increases when either their thickness increases or/and the grain size decreases. Because the grain boundaries significantly influence some physical properties in nanostructured materials, for example thermal and electrical conductivity, coercive field and magnetic losses, the modelling of their structure is thus an important task. The presence of grain boundaries can be evidenced from either diffraction experiments, spectroscopic local probe techniques or magnetic measurements [2–4] or a combination of these techniques, and observed by high resolution transmission electronic microscopy. In the case of Mössbauer spectrometry, it remains a quite difficult task [5]. But in previous studies [6], it has clearly indicated the existence of two components of comparable volume fraction with different magnetic behaviours, as in nanostructured metallic [7] and fluoride [8,9] powders. But let us note that the structure of grain boundaries was controversially debated for example in the case of milled iron nanostructured powders [10–13]. Because the atomic structure modelling of grain boundaries remains an open question, further approaches based on computer calculations have thus to be proposed.

In the present study, we restrict ourselves to the following system: a double or triple grain boundary constrained in between grains which consist of pure perfectly crystalline bcc iron of a 10 nanometer size on average, as experimentally measured in our metallic iron powders prepared by high energy ball milling [14,15]. Eventual dislocations or stresses inside the crystalline grains are

[a] e-mail: greneche@univ-lemans.fr

supposed to have relaxed (or the grains to have been slightly annealed) and are then neglected.

We then have to address the atomic modelling of such a system in an out of equilibrium metastable state, induced by the mismatch of the individual crystalline structure of the grains far from the interfaces.

It is also important to emphasize that great care has to be taken in the simulations: indeed, the well established classical simulation methods, either molecular dynamics or Monte-Carlo simulated annealing, quickly lead to the lowest energy state, namely the infinite crystalline bulk. Various assumptions have then to be made. As in previous works [16,17] molecular dynamics simulations were at first considered to describe a shock in between two crystalline grains; but such an approach involves a huge numerical cost due to the computation of the different forces, as well as a high number of parameters to be assumed such as the initial relative speed of the crystalline blocks, the time to stop the simulation in order to reach a physically realistic state or an annealing law and a constraint on the temperature in order not to reach a gaseous system.

Those constraints led us to prefer a Monte-Carlo simulation with the Metropolis algorithm which does require less parameters and assumptions. Besides, we have developed two different ways to model the interface whose assumptions and parameters are independent, the results of which are very close and do not change when the non fundamental parameters (such as those of the potential) are varied in a reasonable range.

2 Theoretical aspects

We selected the well-established Embedded Atom Method (EAM) to compute the total energy of the system considered.

The first difficulty in the use of this approach is the choice of the potential functions. Several many-body interatomic potentials for Fe have been reported in the literature [18–22]. In a previous study [23], Simonelli and coworkers have developed an interatomic potential for Fe to test various point defects. These potentials give the correct elastic constants of iron. Recently, Byeong et al. [24,25] have however shown that the MEAM (modified embedded atom method) exhibits some critical short-comings. For instance the surface energy of the (111) surface computed on many bcc metals is smaller than the one of the (100) surface. This is in contradiction with experimental results [26,27]. A more general discussion of many-body interatomic potentials for bcc transition metals is reported also by Pasianot and coworkers [28].

In our study, we used the Yang and Johnson parametrization [29], which gives correct structure stability and good results for surface energies and vacancy formation energy. In addition the results showed that these potentials are able to describe accurately both bcc and fcc structures, which can be crucial for an accurate description of grain boundaries. We could reproduce, using periodic boundary conditions and a standard Metropolis simulated annealing method, the bcc and fcc structures of bulk Fe.

3 Computational aspects

Let us first choose a simulation box large enough to contain several nanometric crystalline grains in order to get relevant structural information on both the interfacial and the granular parts of such systems. Before annealing with the Metropolis algorithm, we have to establish initial conditions leading to a physically plausible result.

3.1 Initial condition

As in other works [30–32] we consider several nucleation centres inside the simulation box. For each centre, Euler angles can be chosen in order to orient the relative crystallographic axes of the nanocrystallites. This arrangement aims to reproduce the nanostructured state. The next step is, by adding atoms to the system, to make the crystallites grow in all directions until the structure reaches a certain limit (with a rather large, arbitrary total number of atoms, as will be discussed further below). This limit is given by the Voronoï cell conditions [33,34]. All the points (atoms) belonging to a Voronoï cell are closer from the nucleation centre included in this cell than to all other nucleation centres. These steps lead to a polycrystalline structure yet unusable for annealing, since some of the atoms are too close from each other; the resulting unphysical excess energy gives rise to numerical unstabilities. In order to get more realistic grain boundaries, we then apply two different relaxation methods, labelled I and II.

3.2 Method I

We remove from the system all atoms which are closer to the grain boundaries than a certain distance d. This results in an empty zone between crystallites. The system is then annealed by a modified Metropolis algorithm where not only the atoms but the whole grains are moved, as will be detailed below.

3.3 Method II

We first remove from the simulation box the atoms leading to an energy contribution exceeding a certain threshold. This choice is somewhat arbitrary, but as will be shown later, it can be a posteriori validated from the results.

3.4 Monte Carlo simulations–constraints

We use the Monte-Carlo simulated annealing scheme with the Metropolis algorithm [35], the initial temperature being fixed at 300 K and then brought to a low temperature (for example 10 K) as in other methods employing a quenching process [36]. As previously discussed, this

scheme actually works so well that it rapidly leads to the lowest free energy configuration for the system, namely a quasi-infinite piece of bulk if periodic conditions are used and the size of the simulation box is chosen to reproduce atmospheric pressure, and a large metallic cluster if those periodic conditions are removed [37]. In practice, this is actually observed in the samples if one waits long enough at ambient temperature (probably a few years at 300 K), or if one gently anneals the systems, say, at about 600 K. The simulation method has then to introduce constraints in order to describe a metastable, non-equilibrium state however stable at extremely long microscopic time scales.

Concerning periodic boundary conditions, one could find certain commensurate tilt and twist angles of two grains compatible with a certain range of simulation box sizes, but on the one hand this approach becomes mathematically very complicated in three dimensions [38] (not mentioning the problem of triple grain boundaries), and on the other hand we want to simulate arbitrarily oriented grain boundaries.

We therefore use the following modification to the scheme: the probability for a given atom to be subjected to the Metropolis algorithm is given by $P(x) = e^{-\alpha x}$, where x is the distance from the considered atom to the nearest interface and α is an adjustable parameter chosen here to vary from 0.5 to 2 in Å^{-1}. This probability law is simulated by comparing to a random number between 0 and 1.

The choice of law $P(x)$ is therefore not fortuitous, as it helps obtaining a system with a smooth varying interface. It can be seen as an elegant way to enforce arbitrary constraints for the system considered. Since at infinite distance we have crystallites with perfect atomic lattices, however with arbitrary relative orientations to which the system will tend to adapt, we therefore get a way to describe any grain boundaries in three dimensions, without recurring to periodic boundaries conditions, and still with a quasi-infinite total number of atoms.

So, we can thus consider that we simulate a very large cluster of iron atoms consisting of two or three grains (with bcc lattice), linked each other by a grain boundary. Only the atomic structure close to the interface (as previously defined) is mainly annealed. However, the atoms located far from the interface have a low but non-zero probability to be moved, in order to describe the metastability on microscopic time scales. A further modification of the Monte-Carlo simulated annealing scheme is used in the first method to construct the initial condition (Method I). In this method previously developed to model a collision in between nuclei, atoms, molecules or clusters [35], we simulate a shock in between grains and the establishment of a boundary to accommodate the mismatch in between the relative crystalline structures of the grains. We modify the scheme by considering a Metropolis step acting on the whole grains relative to their common centre of gravity by applying the function of probability according to two different manners at a constant temperature $T = 100$ K, relaxing simultaneously the system during the displacement of the blocks or bringing closer the blocks first, then relaxing the system. The net effect is thus to bring the grains together (corresponding to a lowering of the total energy), the process stopping when the grains are in optimal contact, with at the same time an annealing of the structure of the grains, leading quickly to a metastable, non-equilibrium state of the system. Because of the similarity of the results of these techniques of simulation, we present only the results obtained after a shift of the blocks followed by relaxation. For the second method (Method II), the system is heated rapidly at $T = 2000$ K, that is above the melting point of the iron. It allows to simulate thus the energy brought to the system during the shock and to introduce some disorder. Then, the system is quenched from $T = 2000$ to $T = 100$ K.

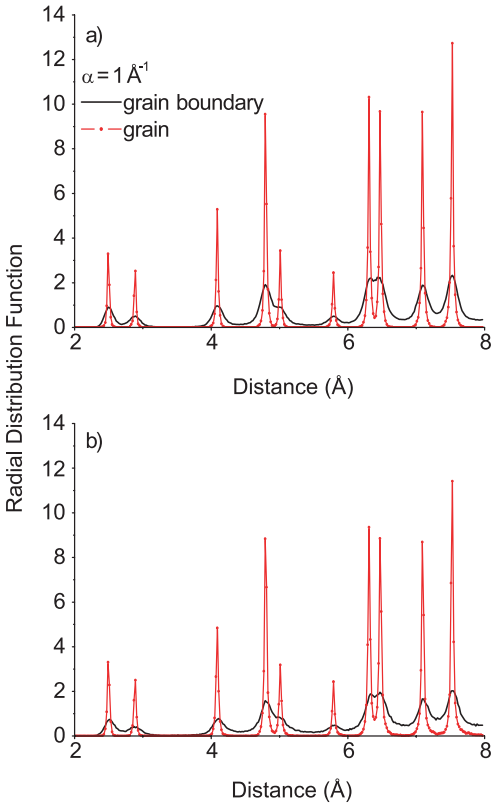

Fig. 1. Comparison of radial distribution functions obtained by taking the histogram of the atomic positions within the interface and within ten atomic layers from the interface (dashed line) for one value of parameter α in method II a), in comparison to method I b).

4 Results and discussion

The following results have been obtained after convergence of the Metropolis annealing procedure, in a box much smaller than the total size of the system in order to avoid finite size and surface effects.

We present in Figure 1, results obtained with a box containing two grains with the two methods for one value of parameter α. In both methods, the relaxation is subjected to the law of transition probability of Boltzmann

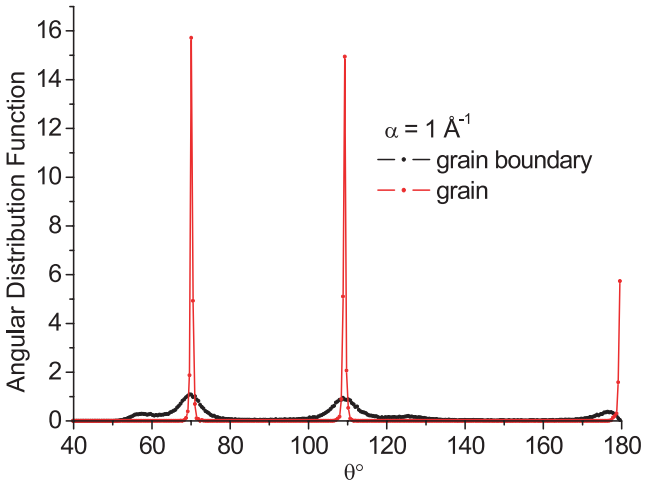

Fig. 2. Angular distribution histogram obtained by taking the histogram of the atomic positions within the interface and within the grain in method I.

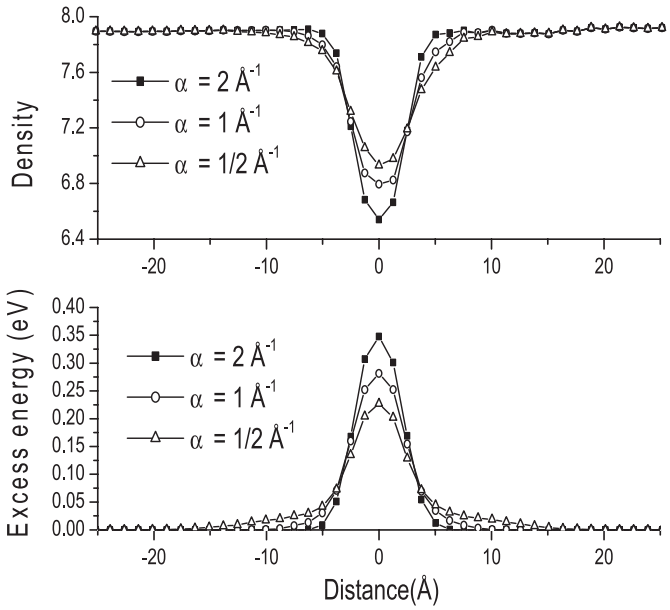

Fig. 3. Evolution of the density and the excess of energy per atom versus the distance with different values of parameter α using method I.

type and 50000 Monte-Carlo steps were performed on a sample containing 65800 atoms, the two grains being disoriented of Euler angles of 5.6, 13, and 22.5 degrees.

As is shown in Figure 1, we reproduce the bcc structure of the grains, as well from the radial distribution histogram computed far from the interface. However, in the grain boundaries, we observe that the characteristic peaks of the radial distribution function of the grain boundary become wider indicating various types of atomic environment. Note that the interface area was selected from 95% of the excess of energy of the whole system. Those results can be interpreted as a kind of a local disorder induced by the excess of energy due to the mismatch of the grains enforced by the constraints. The mismatch of the grains induces disorder at the interface.

To elucidate the presence of the disordered structure in the grain boundaries, we determined the angular distribution histogram of the system (see Fig. 2). We observe on the curve of the grain boundaries a widening and the appearance of two peaks around 55° and 125°. In agreement with Figure 1, the angular distribution histogram reveals the presence of short-range order with distorted entities. Contrarily to the studies performed on pure iron obtained by high energy ball milling by Hernando et al. [10,39], the present simulation results indicate that the structure of the grain boundary can not be described with a structure of the fcc type structure because of the absence of the 90° peak although the EAM potential is able in principle to reproduce this structure.

We have used various reasonable values of parameter α range of the exponential) in order to emphasize its small influence on the result, as long as α is not too small (less than two inverse atomic lattice parameters). Indeed, such a situation which would result in too sharp an interface and therefore without relaxation of the outer core of the grains due to the interface, leading to too large an excess of energy.

Table 1. Thickness of the grain boundaries obtained after relaxing of the system.

α (Å^{-1})	2	1	1/2
Thickness (nm)	0.8	0.8	1

After obtaining the angular and radial distribution histogram of the interfacial zone, we calculated the excess of energy and the density of the system on intervals of constant thickness, along to the normal direction of the interface [40–42]. In Figure 3, we note that the excess of energy curves have a symmetrical, centred maximum, indicating the loss of crystallinity within the grain boundaries. In parallel, it should be noted that this loss of crystallinity is accompanied by a density reduction of approximately 10% inside the grain boundary, in agreement with a previous study [42].

In addition we have used these two curves to estimate the thickness of the grain boundaries by measuring the half-height width versus α. The values obtained are summarised in Table 1: it can be noted that the obtained value of about 0.8 nm to 1 nm is quite small. In addition, it perfectly agrees with the experimental value of 0.7–0.8 nm, i.e. 2–3 atomic layers, as extrapolated from X-ray diffraction [14,15].

Figure 4 shows the evolution of the coordination number in the grain boundaries. The cut-off for the first neighbour computation was chosen from the first peak of the radial distribution histogram located at a distance of 2.65 Å, atributed to the first neighbours. The interface area was selected from 95% of the excess of energy in order not to overestimate the contribution of the crystalline part (eight neighbours), for instance at ± 3.5 Å.

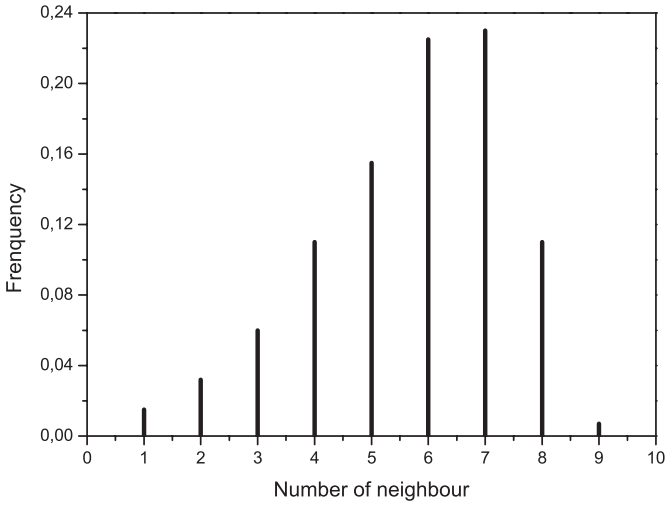

Fig. 4. Distribution of the number of neighbour after the releasing of the system within method I.

As we can notice, the frequency of the numbers of neighbours lower than 2 and higher than 8 is weak but remains greater than zero. This frequency would be modulated a little if we change the cut-off in the nearest neighbour search. On this example, the average value of the number of neighbours is 5.7.

Besides, it can be seen in Figures 1 and 3 that the choice of methods to establish the initial conditions (Methods I and II) have no significant effect on the resulting structure of the interface. As previously stated, one can therefore consider the results free either from the parameter α, the probability of whole block motion versus single atom motion, or from the method used to construct the initial condition and to constraint the system. We further emphasize the flexibility of the simulation methods discussed here by presenting on the results obtained for triple grain boundaries. Those results are close to the ones obtained for two grains, with a further washing out of the peaks due to additional excess of energy due to the presence of the two grains. The method could be readily expanded to a system containing a large number of grains.

5 Conclusions and perspectives

We have presented a new method to compute the structure of nanoscale grain boundaries. The method, based on simple modifications of the Metropolis algorithm inspired from previous work in nuclear or cluster collisions, allows one to address double and triple grain boundaries with arbitrary relative disorientations without recurring to periodic boundaries conditions. The number of simulation parameters is also reduced by comparing the results of two methods to establish the initial condition of the simulation, and to end up with a much simpler scheme than molecular dynamics, which would require several further assumptions, involving thus a higher numerical cost. It is also important to emphasize that we restricted our present discussion on the basis of one relative disorientation, since some arbitrary ones were tested, giving rise to similar results (radial and angular distribution functions). Nevertheless, particular disorientations were also considered: in the case of Euler angles of (0,0,0), a pure crystalline structure is obviously obtained after applying present methods.

The method could then be applied to a system with a large number of grains, or quasi-statically study fracture by moving the boundaries grains slowly apart. It is to be noted that the methods we present here could also be applied to the modelling of epitaxial heterostructures around the interfaces, surface reconstruction, and also crystalline structure containing defects (impurities, vacancies) to a better understanding of their mutual effects.

The structure of the grain boundaries obtained with these methods can be described like a slightly disordered zone with a small thickness within two or several nanocrystals of bcc structure. Indeed, the analysis of the distribution of the number of neighbours shows the existence of a disorder and the angular distribution can not be assigned to a particular structure.

The non-equilibrium distribution of atomic positions resulting from our computations could also be used as input for other programs to compute magnetic or electric properties of the system. We also decided to study iron given the readiness of experimental results obtained with Mössbauer spectrometry, but the method could be applied to simpler systems such as ionic nanostructures or even model systems such as Lennard-Jonesium (LJ).

The various C++ and Fortran 90 programs used in this paper (for computations and visualization) are available upon request to the authors.

We thank F. Calvo for fruitful suggestions, as well as S. Maillet, M. Buard and C. Rödl for developing prototype LJ implementations of the methods.

References

1. R.W. Siegel, Nanostruct. Mater. **3**, 1 (1993)
2. U. Herr, J. Jing, R. Birringer, U. Gonser, H. Gleiter, Appl. Phys. Lett. **50**, 472 (1987)
3. X. Zhu, R. Birringer, U. Herr, H. Gleiter, Phys. Rev. B **35**, 9085 (1987)
4. M. Fitzsimmons, J. Eastman, M. Müller-Stach, G. Wallner, Phys. Rev. B **44**, 2452 (1991)
5. G. Riexecker, Solid State Commun. **122**, 299 (2002)
6. S.J. Campbell, H. Gleiter, Mössbauer Spectrometry Applied to Magnetism and Materials Science, edited by G. Long, F. Grandjean, **1**, 241–303 (1993)
7. J. Balogh, L. Bujdoso, D. Kaptas, T. Kemeny, I. Vincze, S. Szabo, D.L. Beke, Phys. Rev. B **61**, 4109 (2000)
8. H. Guérault, J.M. Grenèche, J. Phys.: Condens. Matter **12**, 4791 (2000)
9. H. Guérault, M. Tamine, J.M. Grenèche, J. Phys.: Condens. Matter **12**, 9497 (2000)
10. L. Del Bianco, A. Hernando, E. Bonetti, E. Navarro, Phys. Rev. B **56**, 8894 (1997)

11. J. Balogh, T. Kemény, I. Vincze, S. Szabo, D. L. Beke, J. Toth, Phys. Rev. B **59**, 14786 (1999)
12. J. Panova, D. Farkas, Materials Research Soc. Symp. Proc., Vol. **364**. MRS, Warrendale, PA, 151 (1995)
13. J. Panova, D. Farkas, Phil. Mag. A **78**, 389 (1998)
14. M. Grafoute, Ph.D. Thesis University of Le Mans (2004)
15. M. Grafoute, A. Slawska-Waniewska, J.M. Grenèche (to be published)
16. M. Hou, V.S. Kharlamov, E.E. Zhurkin, Phys. Rev. B **66**, 195408 (2002)
17. R. Meyer, MRS Symposium Proceedings **634** B8.8.1 (2000)
18. M.S. Daw, M. I. Baskes, Phys. Rev. B **29**, 6443 (1984)
19. M.S. Daw,S. M. Foiles, Phys. Rev. B **35**, 2128 (1987)
20. R.A. Johnson, Phys. Rev. B **37**, 3924 (1987)
21. M.S. Daw, Phys. Rev. B **39**, 7441 (1988)
22. S. M. Foiles, J.B. Adams, Phys. Rev. B **40**, 5909 (1988)
23. G. Simonelli, R. Pasianot, E. Savino, in Materials Research Society Symp. Proc., Vol. **291**, MRS, Warrendale, PA, 567 (1993)
24. L. Byeong-Joo, M.I. Baskes, Phys. Rev. B **62**, 8564 (2000)
25. L. Byeong-Joo, M.I. Baskes, K. Hanchul, C. Yang Koo, Phys. Rev. B **64**, 184102 (2001)
26. B.E Sundquist, Acta Metall. **12**, 67 (1964)
27. H.E Grenga, R. Kumar, Surf. Sci. **61**, 283 (1973)
28. R. Pasianot, D. Farkas, E.J. Savino, Phys. Rev. B **43**, 6952 (1991)
29. Z. Yang, R.A. Johnson, Modelling Simul. Mater. Sci. Eng. **1**, 707 (1993)
30. Van Swygenhoven et al. Phys. Rev. B **58**, 11246 (1998)
31. J. Schitz, F. Di Tolla, K. Jacobsen, Nature (London) **391**, 561 (1998)
32. V. Yamakov, D. Wolf, S.R. Phillpot, A.K. Mukherjee, H. Gleiter, Nature Materials **1**, 45 (2002)
33. G. Voronoi, J. Reine Angew. Math. **134**, 198 (1908)
34. S. Jakob, D.T. Francesco, W.K. Jacobsen, Nature **391**, 561 (1998)
35. F. Calvo, Annales de Physique France, **24**, (1999)
36. P. Keblinski, D. Wolf, S.R. Phillipot, H. Gleiter, Scripta Mater. **41**, 631 (1999)
37. C.L. Cleveland, W.D. Luetke, U. Landman, Phys. Rev. Lett. **81**, 2036 (1998)
38. V. Coffman, E. Iesulauro, J. Sethna, A. Ingraffea (private communication)
39. L. Del Bianco, C. Ballesteros, J.M. Rojo, A. Hernando, Phys. Rev. Lett. **81**, 4500 (1998)
40. P. Keblinski, S.R. Phillpot, D. Wolf, H. Gleiter, Acta Mater. **45** 987 (1997)
41. D. Wolf, J. Wang, S.R. Phillpot, H. Gleiter, Phys. Rev. Lett. **74**, 4686 (1995)
42. J.K. Chen, D. Farkas, W.T. Reynolds JR, Acta. Mater. **45**, 4415 (1997)
43. K.L. Merkle, D.J. Smith, Phys. Rev. Lett. **59**, 2887 (1987)