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A novel hybridised nearly-free-electron tight-binding-bond approach to interatomic forces in disordered transition-metal alloys: application to the modelling of metallic glasses

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Abstract. We present a novel hybridised nearly-free-electron tight-binding-bond approach to interatomic forces in topologically disordered transition-metal alloys and a first application to the atomistic simulation of transition-metal glasses.

Over the last few years there has been increasing interest in the development of interatomic force fields for atomistic simulations (see, e.g., [1, 2]). For the s,p-bonded metals and alloys, reliable interatomic potentials may be derived from pseudopotential perturbation theory [3]. For the d-bonded transition metals a tight-binding (TB) description of the electronic structure is in many ways more appropriate than a free-electron picture [4]. Very recently it has been shown that the total energy of a d-electron system may be written within a tight-binding-bond (TBB) approximation as [5]

$$E_d = \frac{1}{2} \sum_{i,j \neq i} \Phi_{d,\text{rep}}(R_{ij}) + \frac{1}{2} \sum_{i,j \neq i; \alpha\beta} h_{\alpha\beta}(R_{ij}) \theta_{ij,\alpha\beta} \quad (1)$$

where $\Phi_{d,\text{rep}}(R)$ is a repulsive pair interaction provided by the electrostatic, exchange-correlation and non-orthogonality contributions to the total energy, and $h_{\alpha\beta}(R_{ij})\theta_{ij,\alpha\beta}$ is the attractive covalent bond energy between orbitals $\psi_{\alpha,i}$ and $\psi_{\beta,j}$ centred at sites i and j . $h_{\alpha\beta}(R_{ij})$ is the hopping integral and $\theta_{ij,\alpha\beta}$ is the bond order [6], i.e. the difference between the number of electrons in the bonding $2^{-1/2}(\psi_{\alpha,i} + \psi_{\beta,j})$ and the antibonding $2^{-1/2}(\psi_{\alpha,i} - \psi_{\beta,j})$ states. The covalent bond energy involves explicitly only two-body terms, but three- and many-body contributions enter via the dependence of the bond order on the local atomic configuration.

The direct application of this concept to transition metals and their alloys involves several serious complications.

(i) The s, p and d partial pressures are both large, but of opposite sign [7]. This indicates that the s-electron contribution to the interatomic forces is non-negligible. However, it is not very well described in a TB picture.

(ii) The bond order may be written as an integral over the imaginary part of the off-diagonal Green function [5]:

$$\theta_{ij,\alpha\beta} = -\frac{2}{\pi} \int_{-\infty}^{E_F} \text{Im} G_{ij,\alpha\beta}(E) dE. \quad (2)$$

$G_{ij,\alpha\beta}(E)$ has to be calculated for a realistic reference configuration.

In this paper we present a novel hybridised nearly-free-electron (NFE) TBB approach to interatomic forces in disordered transition-metal alloys, with an application to the simulation of the structure of metallic glasses. Pseudopotential perturbation theory is used to write the s-electron contribution to the total energy as the sum of a volume energy and a pair-interaction term with a central pair potential $\Phi_s(R)$. The d-electron contribution is treated in a TBB approximation. s-d hybridisation is taken into account in an approximate way by setting the numbers N_s and N_d of s and d electrons for each component equal to the values resulting from a self-consistent electronic structure calculation for the crystalline metal.

The determination of the bond order potential requires the calculation of the diagonal and off-diagonal Green functions for an appropriate reference configuration. We chose a Bethe lattice (or Cayley tree) [8–10] with a coordination number $Z = 12$, a random occupation of all sites and a single orbital per site (i.e. we assume the d orbitals with different magnetic quantum numbers to be degenerate and neglect the directionality of the d bonds, which seems to be legitimate for a liquid or glassy system). Restricting all interactions to nearest neighbours only, a closed system of equations may be constructed for the transfer matrices S_{IJ} defined by $G_{i,0} = S_{IJ}G_{i-1,0}$ (where I and J stand for the occupation of neighbouring sites i and $i - 1$ by A and B atoms)

$$S_{II} = h_{II}[E - \varepsilon_I - (Z - 1)h_{II}(c_I S_{II} + c_J S_{JJ})]^{-1} \quad (3a)$$

$$S_{IJ} = (h_{IJ}/h_{II})S_{II} \quad I, J \equiv A, B; I \neq J \quad (3b)$$

where the ε_I are the on-site energies and $h_{IJ} = h_{JI}$ the hopping integrals. Equations (3a) and (3b) may be reduced to a cubic equation and solved analytically. The diagonal and off-diagonal Green functions are then given by the standard relations

$$G_I(E) = (E - \varepsilon_I - \Sigma_I)^{-1} \quad I \equiv A, B \quad (4a)$$

$$\Sigma_I = Zh_{II}(c_I S_{II} + c_J S_{JJ}) \quad I \equiv A, B; J \neq I \quad (4b)$$

$$G_{IJ}(E) = S_{IJ}G_J(E) \quad I, J \equiv A, B \quad (4c)$$

with the self-energies Σ_I . This completely determines the bond order potential.

Hence the construction of the effective interatomic interactions proceeds by the following steps.

(i) Determination of the pseudopotential and TBB parameters for the pure metals. The number N_s of s electrons and the number N_d of d electrons are taken from a band-structure calculation for the crystalline metal [11]. The average canonical hopping integral [12] $h_{II}(R_{ij}) = [(dd\sigma^2 + 2dd\pi^2 + 2dd\delta^2)/5]^{1/2} = \sqrt{14}(\frac{2}{3})W_{d,I}(R_a/R_{ij})^5$ is adjusted to the width $W_{d,I}$ of the d band (R_a is the atomic radius at room temperature); $h_{IJ} = (h_{II}h_{JJ})^{1/2}$. The on-site energy ε_I is calculated for the electronic configuration s^1d^{N-1} of the free atom. The s-electron pseudopotential is modelled by an empty-core potential with core radius R_c fitted to the zero-pressure condition [3]. Screening is treated in the Ichimaru–Utsumi [13] approximation to the dielectric function of the electron gas. Numerical values of all parameters for the alloys Ni–Y and Nb–Zr are given in table 1.

(ii) Self-consistent TB Hartree–Fock calculation of the electronic structure of the random A–B alloy on the Bethe lattice, using standard values for the intra-atomic and interatomic Coulomb integrals ($u_{ss} = 0.5$ eV, $u_{sd} = 0.75$ eV, $u_{dd} = 1.6$ eV and $V = 0.25$ eV) [14]), and respecting the constraint of local charge neutrality, i.e.

$$\delta N_{s,I} + \delta N_{d,I} = 0 \quad (5a)$$

and the constraint of a constant total number of d electrons, i.e.

Table 1. Parameters for the effective interatomic potentials, density n and bond orders θ_{IJ} for $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Nb}_{50}\text{Zr}_{50}$ alloys, with pure-metal reference values given in parentheses. See text for details.

	$\text{Ni}_{33}\text{Y}_{67}$			$\text{Nb}_{50}\text{Zr}_{50}$		
	Ni	Y		Nb	Zr	
R_c (Å)	0.58	1.27		1.22	1.22	
N_s	1.09 (1.40)	1.51 (1.31)		1.20 (1.29)	1.39 (1.30)	
N_d	8.91 (8.60)	1.49 (1.69)		3.80 (3.71)	2.61 (2.70)	
ε (Ryd)	-0.34 (-0.36)	-0.14 (-0.13)		-0.23 (-0.24)	-0.19 (-0.18)	
W_d (Ryd)	0.278	0.485		0.716	0.616	
R_a (Å)	1.377	1.991		1.625	1.771	
n (Å ⁻³), liquid		0.0356				
n (Å ⁻³), amorphous		0.0389			0.0485	
	Ni-Ni	Ni-Y	Y-Y	Nb-Nb	Nb-Zr	Zr-Zr
θ_{IJ}	-0.40	-1.85	-1.25	-2.613	-2.242	-1.823

$$c_A \delta N_{d,A} + c_B \delta N_{d,B} = 0 \quad (5b)$$

($\delta x_I = x_I - x_I^0$ stand for the change in the quantity x_I in the alloy relative to its pure-metal reference value). It may be shown that under the constraints (5a) and (5b) the contribution of the promotion energy

$$E_{d,\text{prom}} = c_A(N_{d,A} \varepsilon_A - N_{d,A}^0 \varepsilon_A^0) + c_B(N_{d,B} \varepsilon_B - N_{d,B}^0 \varepsilon_B^0) \quad (6)$$

to the alloy energy is compensated to first order in $\delta N_{d,I}$ by the change in the intra-atomic d-d and s-d interactions, except for a site-diagonal term

$$E_{d,\text{prom}} + E_{\text{intra}} = c_A \delta N_{d,A} \varepsilon_A^0 + c_B \delta N_{d,B} \varepsilon_B^0 \quad (7)$$

which may be combined with the volume energy.

(iii) Calculation of the effective pair interactions. Combining the pseudopotential approach with the s-electron interactions and the TBB approach with the d-electron bonding we find that the total energy of the A-B alloy assumes the form of a volume energy and a pair interaction term

$$E_{AB} = E_{\text{vol}} + \frac{1}{2} \sum_{I,J} \sum_{i(I),j(J)=i(I)} \Phi_{IJ}(R_{ij}) \quad (8)$$

with

$$\Phi_{IJ}(R) = \Phi_{s,IJ}(R) + \Phi_{d,\text{rep},IJ}(R) + \Phi_{d,\text{bond},IJ}(R) \quad (9a)$$

$$\Phi_{d,\text{bond},IJ}(R) = h_{IJ}(R)\theta_{IJ} \quad (9b)$$

and the well known standard expressions for the s-electron [3] and repulsive d-electron [15, 16] contributions. The double sum in (8) extends over sites i, j occupied by I, J atoms. The total effective pair potential in (9a) and (9b) is calculated for the self-consistent number $N_{s,I}$ of s electrons, self-consistent number $N_{d,I}$ d electrons, on-site energies ε_I and bond orders θ_{IJ} resulting from step (ii); see table 1. Note that both the

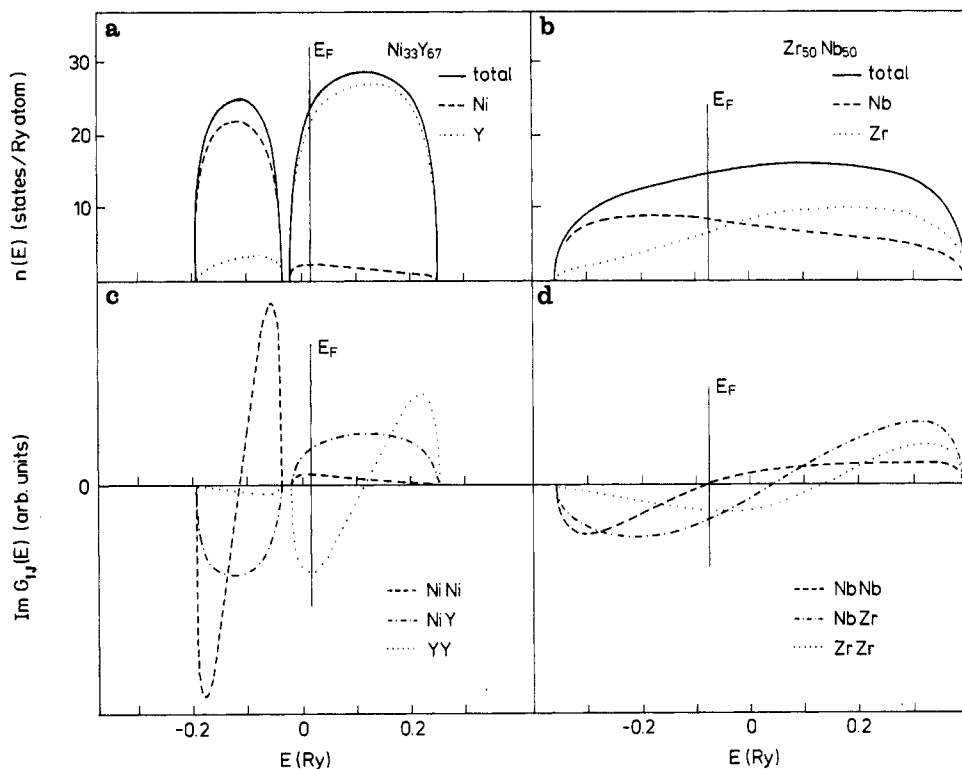


Figure 1. (a), (b) Total and partial d-electron DOSs and (c), (d) imaginary part of the off-diagonal Green functions for (a), (c) $\text{Ni}_{33}\text{Y}_{67}$ and (b), (d) $\text{Nb}_{50}\text{Zr}_{50}$ alloys.

s- and the d-electron contributions to the interatomic interaction will be weakly density dependent. The numbers given in table 1 refer to the solid phase.

As representative examples we treat Ni–Y and Nb–Zr alloys. The Ni–Y phase diagram [17] is characterised by a deep eutectic minimum at the composition $\text{Ni}_{33}\text{Y}_{67}$, the formation of eight intermetallic compounds with compositions ranging from Ni_{17}Y_2 to NiY_3 , and the formation of metallic glasses in a wide composition range centred at the eutectic. The phase diagram of Nb–Zr shows unlimited liquid and solid solubility at temperatures $T \geq 1200$ K. From the point of view of the electronic structure the essential difference between the two alloys is that in Ni–Y the difference in the electronic d levels is of the same order as the average bandwidth, i.e. $|\varepsilon_{\text{Ni}} - \varepsilon_{\text{Y}}| \approx W_d$, whereas, in Nb–Zr, $|\varepsilon_{\text{Nb}} - \varepsilon_{\text{Zr}}| \ll W_d$. As a consequence the electronic density of states (DOS) of Ni–Y is close to the split-band limit, with the lower part of the d band dominated by the Ni states and the upper part by the Y states (that the bands are actually separated by a narrow gap is an unimportant artefact of the Bethe lattice approximation). The DOS of Nb–Zr on the other hand is a good example for a common-band alloy with largely overlapping subbands (figures 1(a) and 1(b)). The form of the band has important consequences for the bond order potential; for a nearly filled sub-band such as Ni in Ni–Y the bonding contributions to θ_{NiNi} from the lower part of the band are almost entirely compensated by the antibonding contributions from the upper part of the band. For θ_{NiY} and θ_{YY} the bonding contributions dominate (figure 1(c) and table 1). For a common-band alloy such as Nb–Zr we find bond orders of about equal magnitude for all three types of bond

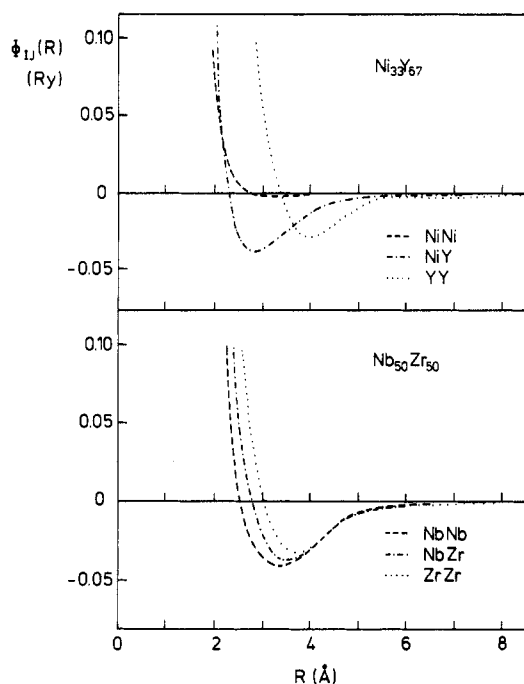


Figure 2. Effective interatomic interactions in $\text{Ni}_{33}\text{Y}_{67}$ and $\text{Nb}_{50}\text{Zr}_{50}$ alloys.

(figure 1(d) and table 1). The differences in the d bands and in the bond orders are reflected in the interatomic potentials (figure 2). In Ni–Y we have a strong covalent contribution to the Ni–Y and Y–Y interactions, but a much smaller one to the Ni–Ni interactions. The Ni–Y potential is much more attractive than the Ni–Ni or Y–Y potentials; its minimum occurs at a distance that is considerably shorter than the mean value of the interatomic distances in Ni and Y (which scale rather well with the position of the minima in Φ_{NiNi} and Φ_{YY}). In contrast to these strongly non-additive potentials the interatomic potentials in Nb–Zr are almost exactly additive in the sense that the Nb–Zr potential is the mean of the Nb–Nb and Zr–Zr interactions.

As stated in the introduction our aim is to construct interatomic force fields for atomistic simulation of topologically disordered (liquid or amorphous) phases. From the form of the potentials it is evident that liquid Nb–Zr will be very close to a regular solution behaviour. The more interesting case is that of Ni–Y, especially in the glassy phase. As in many of the early-transition-metal–late-transition-metal ($T_{\text{E}}-T_{\text{L}}$) glasses, a strong tendency to short-range order (SRO) has been observed in $\text{Ni}_{33}\text{Y}_{67}$ by neutron diffraction with isotopic substitution [18]. $\text{Ni}_{33}\text{Y}_{67}$ shows probably the strongest SRO among all $T_{\text{E}}-T_{\text{L}}$ glasses. Using the potentials shown in figure 2, we have performed a molecular dynamics simulation of amorphous $\text{Ni}_{33}\text{Y}_{67}$, starting from the liquid phase. After reaching equilibrium the liquid is compressed to the glassy phase (Vegard's law is assumed to hold for both liquid and solid phases) and re-equilibrated. Finally the alloy is quenched at constant volume with a quench rate of 10^{14} K s^{-1} (details of the simulation will be reported elsewhere [19]). The resulting partial structure factors are shown in figure 3, together with the experimental data. It is quite surprising that almost all details of the very complex structure factors are well reproduced by the simulation; strong peaks in the Ni–Ni and Y–Y structure factors at $q = 1.8 \text{ \AA}^{-1}$ and $q = 2.0 \text{ \AA}^{-1}$ are almost coincident with a deep minimum in the Ni–Y structure factor at $q = 1.8 \text{ \AA}^{-1}$. The peak

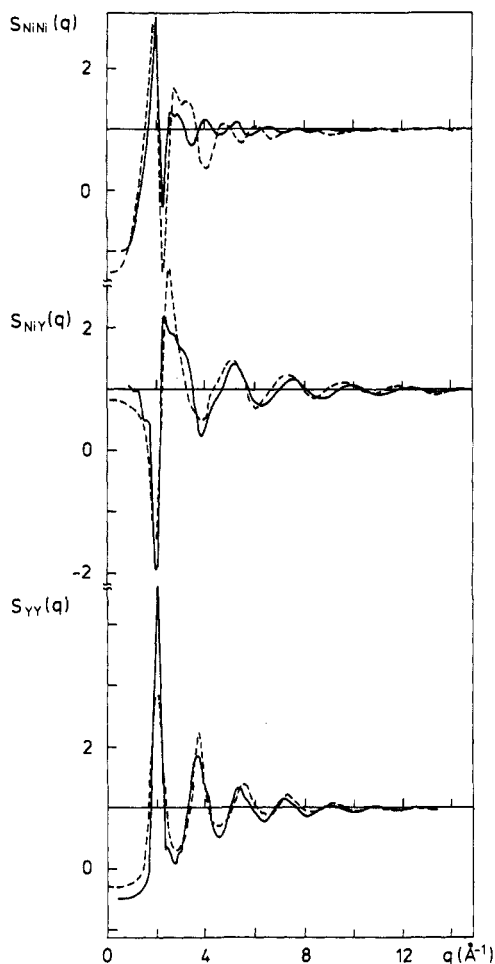


Figure 3. Partial structure factors $S_{\text{NiNi}}(q)$, $S_{\text{NiY}}(q)$ and $S_{\text{YY}}(q)$ for the metallic glass $\text{Ni}_{33}\text{Y}_{67}$: —, molecular dynamics simulations using the potentials shown in figure 2; ---, neutron diffraction [18].

in S_{NiNi} cannot be attributed to the shortest Ni–Ni distances but, together with the minimum in S_{NiY} , indicates rather strong chemical SRO [18]. The form of the partial structure factors is rather far from that of a random packing model (even allowing for the large size ratio) and points to a certain topological SRO as well. A detailed discussion of the model must be left to a forthcoming publication.

In summary, we have developed a novel hybridised NFE TBB approach to interatomic forces in disordered transition-metal alloys. We think that the dependence of the effective pair interaction on the bond order determined by the shape of the d band constitutes an important improvement as it reflects the main physical trends in the interatomic forces as a function of the group-number difference of the components. First applications to the atomistic simulation of the structure of transition-metal glasses look rather promising.

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