Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Fitting electron density as a physically sound basis for the development of interatomic potentials of complex alloys

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1. **Parameterisation process**

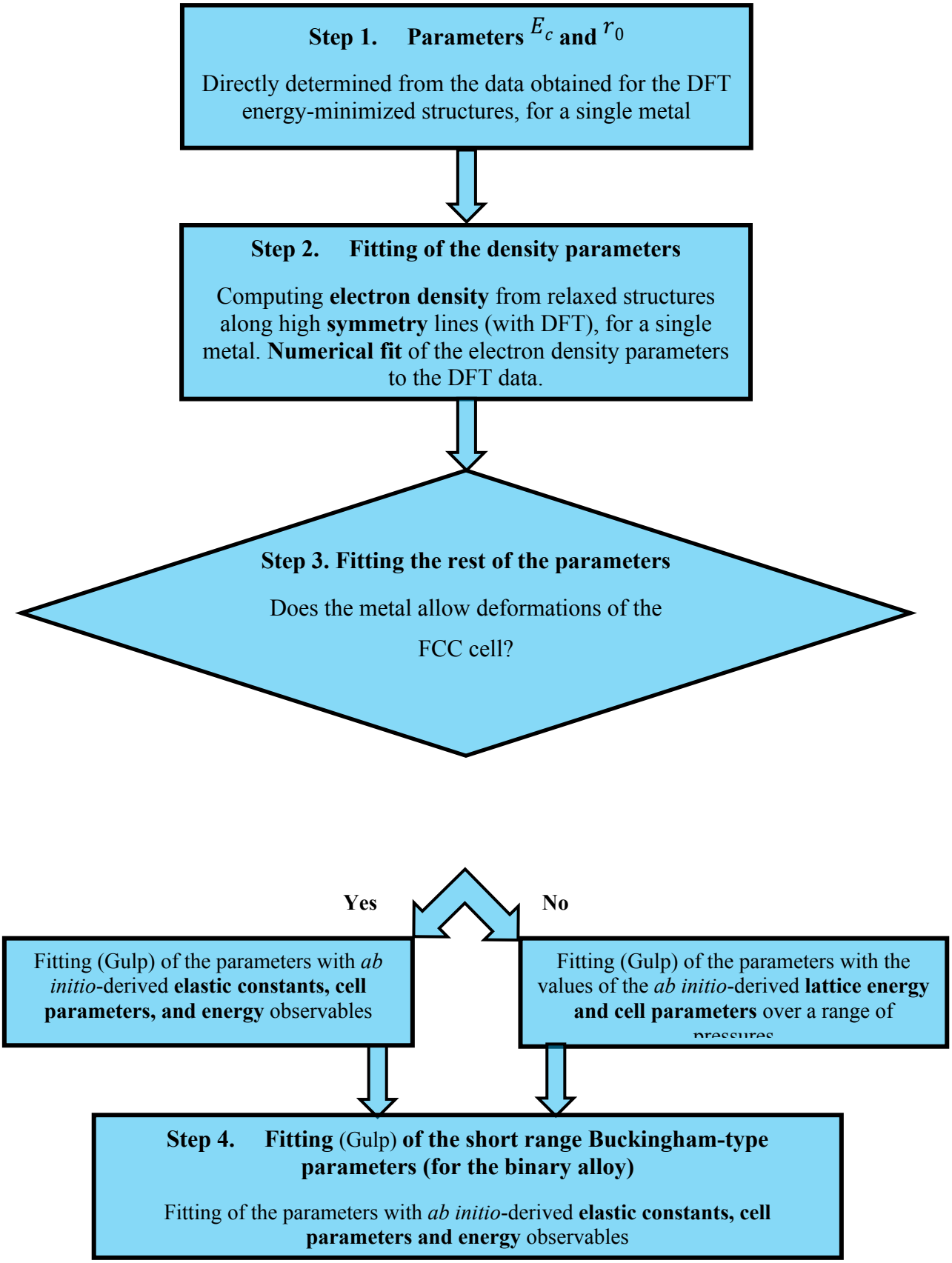

Figure S1. Algorithm developed to carry out the fitting of the potential parameters of the alloy.

2. Simulation of the thermal expansion

Table S1. Simulated and experimental cell parameters of Inconel 625 (Ni-Cr-Mo-Fe).

Temp. (K)	Force field	Exp1	Exp2	Exp3	Exp4	Exp5
120	3.612	3.590	3.591	3.592	3.594	3.598
160	3.613	3.592	3.593	3.594	3.596	3.600
212	3.616	3.594	3.595	3.596	3.598	3.602
296	3.620	3.598	3.600	3.601	3.603	3.607
332	3.622	3.600	3.602	3.602	3.604	3.608
368	3.624	3.602	3.603	3.604	3.606	3.610
468	3.630	3.608	3.609	3.610	3.612	3.616
534	3.634	3.611	3.613	3.614	3.616	3.620
566	3.636	3.613	3.614	3.615	3.617	3.621
626	3.640	3.617	3.618	3.619	3.621	3.625
652	3.641	3.618	3.619	3.620	3.622	3.626
684	3.643	3.620	3.621	3.622	3.624	3.628
712	3.645	3.622	3.623	3.624	3.626	3.630
776	3.649	3.626	3.627	3.628	3.630	3.634
814	3.653	3.628	3.629	3.630	3.632	3.636
848	3.655	3.630	3.631	3.632	3.634	3.638
878	3.657	3.632	3.633	3.634	3.636	3.640
952	3.662	3.637	3.638	3.639	3.641	3.645
988	3.666	3.639	3.640	3.641	3.643	3.647

3. Calculation of the elastic constants

For the determination of the elastic constants, NVT simulations were conducted at the equilibrium volume values determined for each temperature by either LD or MD simulations. The simulations were carried out in the temperature range from 0 to 1000 K, at discrete steps of 100 K. At each temperature, the simulation was stabilized during the first 6 ps, and 14 ps were used for computing the elastic properties, sampling the data each 0.01 ps [7,8].

. The crystal orientation with respect to the Cartesian coordinates is shown in Figure 2. For each temperature, an initial compressive strain of ϵ_{xx}^{0}= -0.5% was applied on the boundary of the cell. The strain was then increased by $\Delta\epsilon_{xx}$= 0.1%, and the same procedure was repeated for every temperature. The strain was successively increased in steps of 0.1%, up to a maximum strain of 0.5%. In this work, two uniaxial deformation test configurations were considered. In the first one, the configuration was x|| [100], y|| [010], and z|| [001]. A uniaxial strain was applied along the x-direction (ϵ_{xx}), and the elastic constants of the crystal (C_{11} and C_{12}) were obtained from:

$$C_{11} = \frac{\sigma_{xx}}{\epsilon_{xx}} \tag{6}$$

$$C_{12} = \frac{\sigma_{yy} + \sigma_{zz}}{2\epsilon_{xx}} \tag{7}$$

where σ_{xx}, σ_{yy}, and σ_{zz} are the normal stresses in the x-, y-, and z-direction, respectively (Figure 2a main text). In the second configuration, the crystal was rotated by 45º around the z-axis for the uniaxial strain test, resulting in x|| [110], y|| [$\bar{1}$10], and z|| [001] (Figure 2b main text). The cell was then deformed along the x-axis and the elastic constant C_{44} was obtained as:

$$C_{44} = \frac{\sigma_{xx}}{\epsilon_{xx}} - \left(\frac{C_{11} + C_{12}}{2}\right) \tag{8}$$

The study of the performance to model systems at a continuum level was performed by means of self-consistent and FFT numerical homogenizations. From single crystal elastic constants, it is possible to determine the polycrystalline elastic behavior by taking into account the so-called Orientation Distribution Function (ODF) of the crystals within the polycrystal, using different analytical or numerical methods.

If the material has no texture (i.e., the ODF is random), the polycrystal will be isotropic and analytical expressions for two independent elastic constants (i.e., either the bulk and shear

moduli, *B* and *G*) are given by different mean field methods [9–11]. For cubic solids, the bulk modulus *K* can be expressed as:

$$K = \frac{C_{11} + 2C_{12}}{3} \tag{9}$$

The shear modulus can be calculated by using the Hill's approximation [12]:

$$G = \frac{G_V + G_R}{2}$$

Where G_V and G_R are the Voigt [13] and the Reuss [14] shear moduli respectively.

This shear modulus can be also computed by solving the following equation:

$$f(G) = 8G^3 + \left(9B + 4G^{'}\right)G^2 - \left(3BG^{'} + 12G^{'}G^{''}\right)G - 6BG^{'}G^{''} = 0 \tag{10}$$

where $G^{'}$ and $G^{''}$ are related to the single crystal elastic constants according to:

$$G^{'} = \frac{C_{11} + C_{12}}{2} \tag{11}$$

$$G^{''} = C_{44} \tag{12}$$

Finally, it is trivial to compute the elastic modulus *E* and the Poisson's ratio ν from *K* and *G* [15]:

$$E = \frac{9KG}{3K + G} \tag{13}$$

$$\nu = \frac{3K - 2G}{2(3K + G)} \tag{14}$$

For a numerical approach of the elastic behaviour of the polycrystal, a home-made computational homogenization FFT code, developed in IMDEA-Materials, was used, called FFTMAD. For these simulations, the accelerated scheme [16] was selected for its very good performance using this phase contrast. The Representative Volume Elements (RVEs) were generated using Dream 3D [17], following a typical log-normal distribution of grains. Around 2000 grains discretized in a cubic box of 128 × 128 × 128 voxels were used. The numbers of grains provide an accurate description of the random texture. The resulting number of voxels per grain (approximately 1000) is enough to provide a good representation of the fields within the superalloy grains [18]. The simulations were carried out imposing a uniaxial strain and the values of the elastic modulus and Poisson's ratio were obtained from the average stress results. For each temperature, ten different RVEs with the same grain distribution were simulated.

Table S3. Simulated monocrystalline elastic constants from MD.

T (K)	C11 (GPa)	C12 (GPa)	C44 (GPa)
1	248.734	176.959	127.911
100	246.141	175.832	127.686
200	240.281	172.210	124.588
300	232.955	167.911	121.833
400	225.697	163.315	116.486
500	218.018	158.131	113.255
600	209.366	152.790	109.031
700	200.877	147.152	105.793
800	192.757	141.867	100.537
900	184.796	137.665	95.306
1000	175.966	131.369	89.953

References

[1] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 169.

[2] J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. (1996).

[3] K. Burke, J.P. Perdew, M. Ernzerhof, Phys. ReV. Lett 78 (1997) 1396.

[4] P. Janthon, S.M. Kozlov, F. Viñes, J. Limtrakul, F. Illas, J. Chem. Theory Comput. 9 (2013) 1631–1640.

[5] S. Plimpton, J. Comput. Phys. 117 (1995) 1–19.

[6] J.R. Davis, ASM Specialty Handbook: Nickel, Cobalt, and Their Alloys, 2000.

[7] D.H. Tsai, J. Chem. Phys. 70 (1979) 1375–1382.

[8] A.P. Thompson, S.J. Plimpton, W. Mattson, J. Chem. Phys. 131 (2009).

[9] L.P. Kadanoff, J. Stat. Phys. 137 (2009) 777–797.

[10] H.M. Ledbetter, R.P. Reed, (1973).

[11] G. Martin, N. Ochoa, K. Saï, E. Hervé-Luanco, G. Cailletaud, Int. J. Solids Struct. 51 (2014) 1175–1187.

[12] R. Hill, Proc. Phys. Soc. Sect. A 65 (1952) 349–354.

[13] W. Voight, Teubner, Leipzig (1928).

[14] A. Reuss, ZAMM-Journal Appl. Math. (1929).

[15] J. Rösler, H. (Harald) Harders, M. (Martin) Bäker, Mechanical Behaviour of Engineering Materials : Metals, Ceramics, Polymers, and Composites, Springer, 2007.

[16] J. Michel, H. Moulinec, P. Suquet, Int. J. (2001).

[17] M. Groeber, M. Jackson, Integr. Mater. Manuf. (2014).

[18] A. Cruzado, B. Gan, M. Jiménez, D. Barba, K. Ostolaza, Acta Mater. (2015).

[19] a. Sarkar, P. Mukherjee, P. Barat, T. Jayakumar, Mahadevan S., S.K. Rai, Int. J. Mod. Phys. B 22 (2008) 3977–3985.

[20] G.K. Dey, S. Albert, D. Srivastava, M. Sundararaman, P. Mukhopadhyay, Mater. Sci. Eng. A 119 (1989) 175–184.

[21] H.K. Kohl, K. Peng, J. Nucl. Mater. 101 (1981) 243–250.

[22] G.P. Dinda, A.K. Dasgupta, J. Mazumder, Mater. Sci. Eng. A 509 (2009) 98–104.

[23] S.K. Rai, A. Kumar, V. Shankar, T. Jayakumar, K.B.S. Rao, B. Raj, Scr. Mater. 51 (2004) 59–63.