Coarse grained Density Functional theory of order-disorder phase transitions in metallic alloys

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The technological performances of metallic compounds are largely influenced by atomic ordering. Although there is a general consensus that successful theories of metallic systems should account for the quantum nature of the electronic glue, existing non-perturbative high-temperature treatments are based on effective classical atomic Hamiltonians. We propose a solution for the above paradox and offer a fully quantum mechanical, though approximate, theory that on equal footing deals with both electrons and ions. By taking advantage of a coarse grained formulation of the density functional theory [Bruno et al., Phys. Rev. B 77, 155108 (2008)] we develop a MonteCarlo technique, based on an \textit{ab initio} Hamiltonian, that allows for the efficient evaluation of finite temperature statistical averages. Calculations of the relevant thermodynamic quantities and of the electronic structures for CuZn and Ni3V support that our theory provides an appropriate description of order-disorder phase transitions.

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Nowadays ground state properties of metallic alloys are routinely calculated by using Density Functional (DF) theory which appropriately incorporates electronic correlations. However, most finite temperature status of art calculations are based on classical Ising models which allow the accurate evaluation of phase equilibria, but are not able to predict the electronic properties. A theory able to cope with both tasks must incorporate quantum mechanics and should be able to explore the very large space of alloy configurations in order to give reliable statistical averages. Unfortunately, quantum simulations as the Car-Parrinello Molecular Dynamics (CPMD) are very hard for the problem at hand and the application of such methods the phase equilibria of metallic alloys seems beyond the capabilities of existing hardware and software. In this Letter we shall outline a straightforward, in this Letter we focus on binary metallic alloys A-B1−c. They shall be studied in the \((T, c)\) statistical ensemble defined by the temperature, \(T\), and the mean atomic concentration, \(c\). In order to have a tractable problem, we shall limit ourselves to the solid state and the normal metal regime or, equivalently, to the temperatures between the superconducting and the melting transitions, \(T_{SC} < T < T_M\). Furthermore, martensitic and magnetic phenomena shall not be considered.

Our first crucial step is to obtain a coarse grained version of the Hohenberg-Kohn DF. If the ions constituting the system are considered frozen on the sites of a simple lattice at their equilibrium positions, \(R_i\), then the electrostatic contribution to the DF can be written as a sum of local terms plus some \textit{bilinear} terms involving the \textit{local moments} of the electronic density:

\[
U^l(\rho(\mathbf{r})) = \sum_i u_i(\rho_i(\mathbf{r})) + \frac{e^2}{2} \sum_{i,j} q_i M_{ij} q_j \tag{1}
\]

In Eq. (1), each lattice site is associated with a Voronoi polyhedron (VP), i.e. to the set of points closer to that particular rather than to any other lattice site, the \(u_i(\rho_i(\mathbf{r}))\) are known functionals of the local electronic density, \(\rho_i(\mathbf{r})\), \(-eq_i\) are the charge multipole moments in each VP and the Madelung matrix, \(M\), is determined by the crystal geometry only. As commented in Ref. [5], the coupling between different VP’s in Eq. (1) is \textit{marginal}, in the sense that it has a simple, analytically tractable form. Most existing approximations for the exchange-correlation energy also consist of sums of local electronic density functionals. However, the local kinetic contributions to the DF are non trivially entangled by the boundary conditions (bc) that the wave-function, or the Green function [6], must match at the VP surfaces. A marginally coupled DF then requires an approximation for the kinetic part. The literature reports several ways in which such decoupling has been obtained: Ref. [7] uses vacuum bc’s, while random bc’s are employed in Ref. [11]. In our approach the \textit{true} bc’s are replaced by appropriate mean field bc’s [6]. The same procedure defines the class of the Generalized Coherent Potential Approximations (GCPA), whose prototype, the Isomorphic CPA (ICPA), has been introduced by Soven [12]. The ICPA provides an excellent picture of the spectral properties of metallic alloys but may lead to incorrect predictions about the electrostatics [14]. Modern GCPA schemes like the Polymorphous CPA (PCPA) heal the shortcomings of the old ICPA model and provide fairly good total energies both for ordered and disordered alloy configurations [4]. We shall then use the
GCPA DF [6]:
\[ \Omega^{GCPA}(\{\rho_i(r)\}, \mu; \{\xi\}) = \sum \omega^\alpha(\rho_i(r)) + \frac{e^2}{2} \sum_{ij} q_i M_{ij} q_j - \mu \sum q_i \]
In Eq. (2), the dependence on the alloy configuration is identified by the set of occupation numbers \( \{\xi\} \), with \( \xi_i = 1 \) (or 0) for sites occupied by an \( A \) (or \( B \)) atom. In the case of a simple lattice, the local functionals \( \omega^\alpha(\rho_i(r)) \) parametrically depend on the site chemical occupation only, \( \alpha = A \) or \( B \). Minimizing Eq. (2) with respect to the \( \rho_i(r) \) provides a set of Euler-Lagrange equations coupled only through the Madelung potentials, \( V_i = \sum_j M_{ij} q_j \), and the chemical potential \( \mu \):
\[ \frac{\delta \omega^\alpha}{\delta \rho_i(r)} + e^2 V_i = \mu \]
Within the alloy sample specified by \( \{\xi\} \), due to Eq. (3) and to the variational properties of the GCPA DF [6, 16, 17], the local charge densities for each chemical component, \( \rho^\alpha(r) \), are unique functions [6] of the Madelung potentials. By virtue of the Hohenberg-Kohn theorem, the same holds for any other local physical observable,
\[ \langle O \rangle_i = O^\alpha(V_i) \]
Evidently, also the charge moments, \( q_i \), are unique functions of the \( V_i \). If, as it can be argued on a physical ground, the \( qV \) laws, \( q_i = q^\alpha(V_i) \), are strictly monotonic [6], then they can be inverted, thus allowing to recast the first term in Eq. (2) as a function of the charge moments rather than a functional of the full charge density, \( \omega^\alpha(\rho_i(r)) \rightarrow \tilde{\omega}^\alpha(q_i) \). This gives the desired coarse graining.
Actually, in the metallic state, the \( qV \) laws are not only monotonic but numerically almost indistinguishable from straight lines [6, 18, 19]. Thus, an excellent approximation for Eq. (2) can be obtained by a series expansion about the zero field (or ICPA) values of the charge moments rather than a functional of the full charge density, \( \omega^\alpha(\rho_i(r)) \rightarrow \tilde{\omega}^\alpha(q_i) \). This gives the desired coarse graining.

In order to test our GCPA-CEF-MC method, we have selected two well studied systems: CuZn [25, 26, 27] and Ni3V [28]. For a binary alloy, it is determined by only three parameters that can be easily obtained by GCPA-DF calculations. In this Letter we implement a coarse grained all electrons theory based on the GCPA DF and a finite temperature Monte Carlo (MC) sampling [21, 22] of the alloy configurations space. This theory, in the following referred to as GCPA-CEF-MC, consists of three major stages [23]: (i) the GCPA DF is determined by \( T = 0 \) electronic structure calculations [24]; (ii) for a given thermodynamic point \( (T, c) \) the relevant ensemble of configurations is sampled by a MC based on the CEF Hamiltonian; for each configuration, the local charges and Madelung potentials are obtained by minimizing Eq. (5), whose solutions are numerically indistinguishable [6] from those of Eq. (2); (iii) the obtained distribution of the Madelung potentials (DMP) (see Fig. 1) then allows for the evaluation of the appropriate ensemble averages for the electronic properties through Eq. (4). As an example, we report in Fig. 2 the electronic density of states (DOS) for CuZn alloys at several temperatures. The stage (ii) of our GCPA-CEF-MC provides the ensemble averages corresponding to the relevant thermodynamic quantities and to the properties related with the atomic degrees of freedom only. Such is, for instance, the atomic Short Range Order (SRO) (see Fig. 3) where results for Ni3V alloys are presented.
It is clear that such impressive figures can be obtained for both alloys thermal expansion has been included \[31\]. This inclusion, however, implies only small quantitative changes to our results. Below \( T_M \), both systems present disordered solid solution phases, based on the relatively open bcc lattice for CuZn and on the close-packed fcc for Ni\(_3\)V. On decreasing \( T \), both systems undergo a transition to the ordered phases, B\(_2\) and DO\(_{22}\) respectively. The phase transitions have been monitored by plotting the total energies and the specific heats \( T \) (Fig. 1). The calculations for CuZn alloys show the neat evidence of an order-disorder transition occurring at \( T_O \approx 465 \text{K} \), with a smooth dependence on \( N \), the number of atoms contained in the simulation box. In the vicinity of the transition, quite large \( N \) values are necessary to obtain well converged thermodynamic properties for the Ni\(_3\)V system. For the largest simulation box, ordering occurs on cooling between 1692.5 and 1690 K, while, on heating, the low-\( T \) ordered state disorders between 1710 and 1712.5 K. Our best estimate for \( T_O \) in Ni\(_3\)V is then 1701 ± 11 K. The transition reveals a first-order character, as confirmed by the abrupt change in the SRO’s displayed in Fig. 3. The sharp first-order features of the transformation are gradually suppressed by finite size effects in the smaller simulation boxes investigated.

Our results demonstrate that the GCPA-CEF-MC theory is able to provide a sensible description of ordering phenomena in metallic alloys. Remarkably, we find complete agreement with the experiment about the low-\( T \) ordered phases and the theory correctly discriminates between first- and second-order transitions. The agreement with the experiment about the ordering temperatures, however, is not completely satisfactory. The experimental ordering temperatures \[32\] for CuZn and Ni\(_3\)V, 740 K and 1313 K, respectively, are in one case lower and in the other higher than the calculated values. This is probably due to the single-site nature of the GCPA and to the approximations \[24\] made for the site potentials.

The methodologies presented in this Letter offer a route to alloy thermodynamics that fully includes electrons and appreciably enlarges the scales at which quantum mechanics can be applied. The calculations here discussed consider up to 2000 atoms and up to \(10^{11}\) local chemical environments for each point in the \((T,c)\) space. It is clear that such impressive figures can be obtained only because we have a fixed crystal lattice. The applica-
FIG. 4: Electronic contributions to the total energies, $E$, and the specific heats, $c_V$, for CuZn (upper frame) and Ni$_3$V (lower frame) alloys as a function of the temperature. The specific heats (insets) identify the ordering temperatures, $T_O$, with the respective uncertainties indicated by the shaded regions, and exhibit the typical $\lambda$-shape. Different symbols refer to different sizes ($N$) of the simulation boxes. CuZn energies do not show hysteresis, as expected for the second order transition bcc-B$_2$. For the largest simulation box, Ni$_3$V energies show a hysteresis loop, revealing the first-order character of the symmetry breaking fcc-DO$_{22}$ transition [23].

The calculations presented have been executed using the computational facilities located at the CINECA (Bologna, Italy) and at the Consorzio COMETA, project PI2S2 (http://www.pi2s2.it).

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