Computational metallurgy and changes of scale / Métallurgie numérique et changements d'échelle

Ab initio approaches to designing alloy phase equilibria

Des calculs ab initio aux diagrammes de phases

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A R T I C L E   I N F O

A B S T R A C T

We present a brief overview of recent *ab initio* based developments to designing bulk thermodynamic properties and phase equilibria for alloys. We also discuss the potential links that exist between *ab initio* methodologies and the Calphad phenomenological approach, in order to build an efficient and predictive tool for the calculation of phase equilibria of complex, multi-component often found in industrial alloys.

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R É S U M É

Nous présentons une réflexion sur l'état de l'art des calculs des propriétés thermodynamiques des alliages et de leurs équilibres de phases à partir de méthodes issues de la mécanique quantique. Nous discutons aussi l'intégration de ces méthodes dans l'approche phénoménologique de type Calphad permettant ainsi d'aborder de manière prédictive l'étude de la stabilité de phases de systèmes multi-composants à applications industrielles.

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1. Introduction

One of the greatest challenges in computational materials science is the ability to design a new material, optimizing the composition and processing steps, in order to determine accurately the properties required for specific technological applications. In parallel with this demand, it has come to be recognised that this can be met efficiently only by achieving a thorough understanding of how atomic, molecular and mesoscopic features influence macroscopic behaviour, and how alloy properties may change with composition, temperature and pressure. *Ab initio* electronic structure theory of 'real materials' aims at understanding materials properties from an atomistic quantum-mechanical point of view, retaining the complexity and specificity of actual materials, without losing track of the basic laws of physics [1]. In particular they give access to properties such as energetics without reference to any experimental data. Recent advances in *ab initio* calculations make it possible to routinely predict accurate thermodynamic data such as lattice stabilities or formation energies of many systems. Moreover, statistical mechanics and computational thermodynamics approaches known as the CALPHAD methodology [2] can use this information as an input to investigate the problem of phase stability as a function of composition, temperature and pressure. Thus such methods appear to offer a way of predicting the thermodynamics of phases and phase equilibria in

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alloys well-suited to supplementing experimental thermodynamics databases of free energies obtained from an optimization process involving experimental thermodynamic data combined with observed phase diagrams.

During the last decades, the development of such predictive approaches have benefited from enormous increases in computing power, coupled with significant advances in the accuracy and efficiency of computational methods. As a result, *ab initio* modelling is starting to pay-off in a dramatic way, bridging the gap between fundamental research and materials engineering. This way of modelling alloy phase equilibria, however, raises some specific questions. *Ab initio* calculations are performed by solving the Schrödinger equation, able to describe the bonding between atoms using only the atomic number of the constituents as an input. The challenge is to find this solution even for complex problems occurring in phase diagrams and to achieve at the same time the exceedingly high accuracy necessary to calculate phase equilibria. The complexity of actual materials occurs at different levels: (a) the number of constituents. Most industrial alloys are multi-component with often more than ten constituents. In principle, *ab initio* calculations are only limited by the number of atoms in the unit cell, but not by the number of constituents in the phase. However, the increase of constituents is often related to the occurrence of some degree of disorder of the underlying crystalline structure leading to complex configurational phenomena. The situation becomes even more problematic in liquids where we have to find the configuration of minimum free energy within a continuum of possible liquid structures. (b) Another complexity is related to the physical contributions to the free energy of a phase. In addition to configurational excitations, other contributions like magnetic, vibrational ones may also play a crucial role in the stabilization of a phase. As this time, a full accounting for all physical contributions and their couplings from *ab initio* calculations is not a straightforward matter.

Predicting phase stability with absolute certainty is currently an intractable problem in materials science. When calculating phase equilibria, we often need to know phase boundaries to within a few Kelvin. Even for simple cases, *ab initio* calculations do not have this exceedingly high accuracy necessary to such determinations.

The complexity of materials, combined with the need to achieve high accuracy, has two important consequences in designing thermodynamic properties from *ab initio* calculations. *Ab initio* calculations can be combined: (a) with statistical mechanics to unravel the main physical contributions to the free energy of a phase and to predict what will happen when composition, temperature and pressure are varying. The main objective is to develop coarse-graining theories that have been so successful in other parts of science; (b) with the Calphad methodology to form a hybrid *ab initio*/computational-thermodynamics method. First, energetic calculations from *ab initio* can be used within Calphad, to supplement or modify existing thermodynamic databases. This is particularly useful when there is little or no information on the phases that take part in equilibria. Second, the coarse-graining theories may be used to develop thermodynamic models that can be implemented in the phenomenological Calphad approach.

In Section 2, we briefly present the density functional theory that is the foundation of modern electronic structure calculations. More particularly, we focus on current limitations of *ab initio* calculations, emphasizing that the accuracy of their predictions may depend critically on their underlying approximations. An excellent and complete summary of electronic structure theories can be found in the recent book by Richard Martin [3]. In Section 3, we discuss the different links between *ab initio* calculations and statistical mechanics to compute not only zero-temperature energetics but also finite-temperature contributions to alloy free energies arising from electronic, configurational and vibrational excitations. In Section 4, we review the potential links that may be established between *ab initio* calculations and the Calphad methodology.

2. *Ab initio* calculations: an overview

The starting point of a quantum theory of materials is the Hamiltonian of the many-ion–many-electron system and the possibility to solve the Schrödinger equation (SE). The first step to reduce the complexity of such a system is the adiabatic approximation which allows one to study the electrons and the lattice dynamics independently. A very important further step was realized in 1964 when Walter Kohn and coworkers [4,5] developed the density-functional theory (DFT) which casts the intractable complexity of the electron–electron interactions into an effective single-particle potential determined by the exchange-correlation functional. Basically, this term incorporates all the difficulties related to the original many-body problem, and the task of finding a functional that embodies the required information seems just as hopeless as that of calculating the exact many-body wave function for hundreds of electrons. What saves this approach is that a very simple-minded approximate functional, like the local-density approximation (LDA) works correctly, at least for metallic systems. However, it has some shortcomings, mostly due to the tendency of overbinding, which cause slightly too small lattice constants (up to 3%) and too high cohesive energies (up to 20%). Recognising that LDA failures must in part be due to ignoring spatial variations in the density, other functionals have been developed that include dependence on the gradient of the density. One approximation along this line, known as the generalized-gradient approximation (GGA), improves predicted binding and dissociation energies. More important is that the correct magnetic ground state is predicted by GGA for ferromagnetic Fe [1]. More generally, the description of the electron–electron interactions can be made by using the hierarchy of functionals proposed within DFT [6]. In those cases where DFT alone does not provide an adequate solution (strong electronic correlations, excited eigenstates, etc.), post-DFT corrections such as many-body perturbation theory [7] or dynamical mean field theory [8] may be used to improve the DFT predictions.

A variety of mature DFT codes are nowadays available to provide an accurate framework for calculating the relative energetics of competing structures in solids and liquids for a wide range of materials. However, DFT calculations are actually limited to structures containing around 500 atoms, while *ab initio* molecular dynamics (AIMD) are practically limited to

time scales less than 1 ns. It is clear that for most cases in materials science, direct applications of DFT to the calculation of thermodynamic properties remain intractable. Effective strategies have nonetheless been developed to bridging the size and time-scale limitations imposed by DFT. In the next section, we present integrated approaches to the design of phase equilibria that combine accurate *ab initio* total-energy calculations and statistical–mechanical modelling. This combination of methods enables parameter-free predictions of the finite-temperature thermodynamic properties governing the phase stability of specific metallic materials like compounds and solid solutions.

3. *Ab initio* thermodynamics

3.1. Thermal excitations

In an ordered non-magnetic solid, thermal fluctuations may come from different contributions like electronic excitations and lattice vibrations, and accordingly the free energy can be written as $F = E_0 + F_{\text{ele}} + F_{\text{vib}}$ where E_0 is the absolute zero total energy. Let us mention that including magnetic contributions in the free energy is still a challenging problem except for simple cases [1]. The electronic contribution can be obtained easily form the knowledge of the electronic density of states and the Fermi distribution [9]. As a rule, this term becomes significant only at high temperatures (beyond ~ 1000 K). The quantum treatment of lattice vibrations in the harmonic approximation provides a reliable description of thermal vibrations for low and moderately high temperatures. Within the harmonic approximation [9,10], the thermodynamic properties are entirely determined by the phonon density of states, i.e. $g(\upsilon)$. The harmonic approximation can be improved by making $g(\upsilon)$ volume dependent, which can be easily done by calculating the phonon density of states for several volumes. This approximation is called the quasiharmonic approximation. However, for the purpose to modelling thermal expansion, it is more convenient to parameterize directly the volume-dependence of the free energy itself:

$$F(T, V) = E_0(V) + F_{\text{ele}}(T, V) + F_{\text{vib}}(T, V)$$

Currently, two different approaches for evaluating vibrational properties of systems from *ab initio* calculations have evolved. Density functional perturbation theory has been implemented mainly in plane wave based density functional codes to obtain force constant matrices directly from linear response expressions [10]. Although the linear response theory is considered to be more accurate and is particularly useful when a system is characterized by non-negligible long-range interatomic forces (ionic solids), the direct force method [10] is easier to use since it can operate with any *ab initio* codes able to accurately compute the forces on atoms. This method is also very appropriate for thermodynamic studies since it allows determining the vibrational properties of complex structures.

Finally, let us mention that while harmonic (or quasiharmonic) theory is known to be highly accurate for a wide class of materials, important cases exist where this approximation breaks down due to large anharmonic effects. Examples include the modelling of ferroelectric and martensitic phase transformations. In this case, direct application of molecular dynamics (MD) offers a general framework to model thermodynamic properties of anharmonic solids [11]. Molecular dynamics can be also used to describe structural and thermodynamic properties in liquid materials. More particularly, recent studies have shown that such approaches can predict a liquid–liquid phase transition in undercooled silicon [12]. Other applications of AIMD have concentrated on the investigation of short-range order in stable and undercooled liquids with the aim of elucidating the ability to form glassy or new crystalline alloys [13,14].

A recent work about the eutectic $Au_{81}Si_{19}$ alloy illustrates the state-of-the-art for this class of *ab initio* simulations. The local structure of the eutectic alloy is found to display a well-defined CSRO that enhances Au–Si interactions in contrast with the solid mixture and may explain the high stability of the liquid phase on the basis of preferential Au–Si bonds [15]. These unusual properties have been used to predict the occurrence of a new crystalline ground state in this system [16] as well as to interpret an important enhanced degree of supercooling of eutectic droplets deposited on an Au-induced (6×6) reconstruction of the Si(111) substrate [17].

3.2. Configurational excitations

The cluster expansion (CE) method [18,19] provides today's start-of-the-art framework to parametrize the energetics of multicomponent systems as a functional of configurational variables on an underlying lattice. It is routinely applied to binary alloys which form an underlying primitive Bravais lattice (e.g. bcc, fcc or hcp) with applications to more demanding problems (complex basic lattices [20], multicomponent systems [21], and surfaces [22]) rapidly growing in number and success. The basic premise of the CE method is that the energetics of different configurations of a given system can be described by an Ising-like framework of pair and multisite interactions. In practice, the method relies on the fact that there is only a finite number of non-negligible interactions, their numerical values being determined by a fit to a finite number of *ab initio* calculated formation energies for different configurations. Once we know these interactions, we can scan many configurations in search for ground states or configurational thermodynamic properties such as phase transitions, short-range order, etc. The cluster expansion thus presents an extremely concise and practical way to model the configurational dependence of the energy of an alloy but choosing exactly the set of interactions which must be retained is not easy. For instance, certain distant pairs or three-body interactions may be more important than nearest-neighbour pairs and the set of "the most efficient" effective cluster interactions (ECI) depends on the alloy. Essentially two different approaches to this

problem are actually used. The first one, known as the hierarchical approach postulates that if a given cluster is included, all other clusters of same size and all subclusters should be included [23]. However, this restriction becomes rapidly impractical unless the series converge after few terms. Van de Walle and Ceder [24] have shown how to make a hierarchy-based approach manageable by introducing cross-validation as a systematic criterion to assess the predictive power of the cluster expansion but adding specific rules to capture "physically meaningful" candidate clusters. An alternative approach developed by Blum and Zunger [25] is to attempt to identify the leading cluster interactions independent of hierarchical constraints. The set of input structures is split into two parts, one for fitting ECIs, and one to check predictions made with these ECIs. The procedure is repeated for different choices of fitting or prediction sets and the average prediction error is the cross-validation score. Very recently, it was shown that the search of leading terms can be efficiently performed using a genetic algorithm [26]. Recently, the study of complex phases, where several inequivalent sites exist in the unit cell, has become a focus of theoretical investigations [20,27,28] based on the technological importance of such phases. More particularly, the site preference in typical Frank–Kasper σ and μ phases for different alloys has been modelled using DFT methods combined with the cluster expansion–cluster variation method. Predicted site occupancies agree well with available experimental data. It was also shown that unlike order–disorder transformations in simple crystal structures, the preferential occupancy of atomic species for particular sites cannot be removed by annealing. Such results allowed us to examine also the validity of the compound energy model widely used in the Calphad methodology to model thermodynamic properties of such complex phases. This will be discussed in the next section.

4. Links between *ab initio* calculations and Calphad

4.1. Data bases

In the previous section, we have presented the most recent advances in *ab initio* calculations that allow accurate prediction of thermodynamic properties, such as formation energies of binary alloys. Furthermore, when the link between *ab initio* calculations and statistical mechanics has been achieved, thermodynamic properties as functions of alloy composition and temperature are also available. All this information can be used to supplement or modify existing databases necessary to the Calphad approach or to make a theoretical assessment "*à la* Calphad" of thermochemistry of alloys [2,29,30]. This combination is particularly desirable for phases of practical interest like metastable precipitate phases which are often absent from experimental thermodynamic databases. This input from *ab initio* adds also to the capabilities of Calphad to predict the thermodynamic properties of complex multicomponent alloys. Additionally, in cases where an experimental controversy exists, *ab initio* calculations can offer a pragmatic tool to solve it. Such an approach may be particularly efficient when the structural stability of intermetallic compounds, like for instance in the Fe–Zr system, is found to be different [31].

4.2. Models

The compound energy formalism (CEF) [32] is commonly used within the Calphad methodology to describe in complex multi-component systems substitutional and interstitial solutions, intermetallic phases with wide homogeneity range, and order/disorder transformations. However, in the case of the Frank–Kasper (FK) phases, modeling the Gibbs energy is still difficult despite the versatility of the Calphad approach. Indeed most FK phases have multiple sublattices (five in the case of the σ and μ phases) and in the CEF one has to consider as many distinct sublattices as there are crystallographic sites. 32 parameters are then needed to model σ and μ phases, but only a few of them can be assessed from experimental information. However, it is possible to calculate all these parameters *via* the possible ordered configurations directly by using *ab initio* calculations [20]. The temperature dependence is then provided by the Bragg–Williams–Gorsky approximation (BWGA) [33], which implies random distributions of species in each crystallographic site, i.e. short-range order is ignored. A comparison with the more sophisticated approach that combines the cluster expansion with the cluster variation method (CVM), made for different alloys and different types [28] of FK phases, i.e. σ and μ phases, indicates that the CEF model is sufficient to describe the temperature and composition dependencies of site occupancies as the CE-CVM calculations. As an example of such methods, the computed phase diagram of the Ni–Nb system is presented in Fig. 1 (solid lines) together with the phase diagram calculated by Bolcavage and Kattner (dashed lines) [34] as well as experimental data used in their assessment and those obtained later by Joubert and Feutelais [35].

5. Conclusion

In summary, the techniques presented in this contribution provide a framework for computing the thermodynamic properties of alloys from DFT calculations. *Ab initio* methods offer the advantage of being able to give estimates of thermodynamic properties in situations where direct experimental measurements are difficult. However, substantial gaps still exist between the largest systems accessible to DFT calculations and the phase stability of multi-component alloys with accuracy comparable to experimental phase diagram measurements. In the simplest cases, as ordered compounds and solid solutions based on a simple lattice, these gaps may be partly overcome by efficient coarse-graining theories. For instance, *ab initio* calculations can be used in conjunction with statistical mechanics to yield finite-temperature thermodynamic properties with accuracy comparable to that achievable experimentally. New tools like the Alloy Theoretic Automated Toolkit (ATAT)
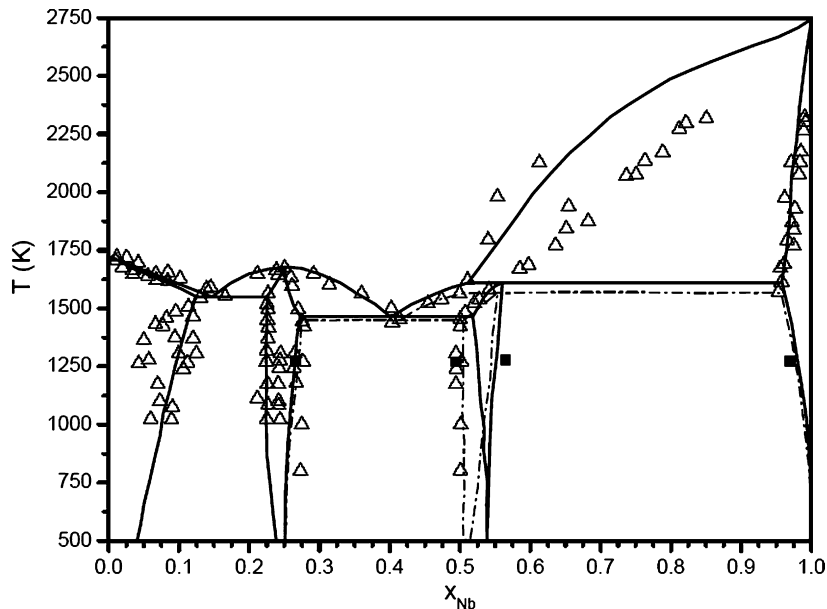
Fig. 1. Calculated phase diagram compared with the one from Bolcavage and Kattner [34] (dashed lines) and the experiments used by them (△) and the more recent ones from Joubert and Feutelais [35] (■).

Fig. 1. Diagramme de phases calculé en couplant les calculs *ab initio* à la technique Calphad (trait plein). En comparaison (trait pointillé), le diagramme de phases calculé par Bolcavage et Kattner [34] à partir de données expérimentales (△) et celles plus récentes de Joubert et Feutelais [35] (■).

drastically simplify the practical use of these methods [36]. For more complex systems, like multi-component industrial alloys, we have presented different routes to integrate *ab initio* calculation in the Calphad methodology. *Ab initio* calculations provide formation and structural energies even for hypothetical structures and in such cases, they have found applications as a framework for augmenting the experimental databases that form the basis of the Calphad approach. Another promising route is to integrate directly *ab initio* calculations into the CEF model commonly used to model complex multi-component systems. With improvements in the accuracy of *ab initio* methods and developments of new coarse-graining techniques, the *ab initio* framework outlined in this article is anticipated to be applied more and more as a computational modeling tool of utmost importance in materials science. More particularly, by predicting the properties of a series of materials before they are synthesized, computational modeling can guide experiments in promising directions, and just as importantly, steer them away from attempts that would be less fruitful.

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