Abstract

Metals are ubiquitous in numerous aspects of our lives, due to the possibility of adjusting their properties to a wide range of technological needs (light-weight, high-strength, durability, etc.). The ability to provide such a large variability in metallic properties is based on a profound knowledge gathered over centuries of research. One might, therefore, be tempted to consider the task of metal research as being completed in general. This is however by far not the case. The reason is the tremendous complexity of such materials at microscopic scales, which is actually the origin of their versatility. This complexity is still poorly understood and most traditional approaches are facing fundamental difficulties in providing further progress.

A very recent approach to enable further progress is so called *ab initio* methods. Their basic idea is to start the materials description directly at the electronic scale, in contrast to many traditional approaches which focus on the meso-/macroscopic scale. The key advantage of *ab initio* methods is their derivation from universal quantum mechanical laws which allow, in principle, to fully incorporate the complexity inherent to metallic materials. The actual application of these methods faces serious challenges: (i) A direct quantum mechanical solution is not feasible and approximations are unavoidable. For instance, the density functional theory (DFT), a particularly successful *ab initio* approach, relies in practical applications on the so called exchange-correlation functional, which cannot be systematically improved. (ii) Despite various approximations, *ab initio* calculations are computationally highly demanding and the development of advanced simulation techniques is needed. (iii) Typically, only $T = 0$ K conditions are considered and the extension to finite temperatures – crucial for metals – is related to even larger CPU requirements.

The general objective of the present work is to address various aspects related to these challenges. For that purpose, a systematic and with respect to numerical accuracy fully controlled DFT study of thermodynamic properties for an extensive set of metals is provided. A special focus is on the assessment of the predictive power of present day's exchange-correlation functionals and on the influence of temperature in the full temperature window from zero Kelvin up to the melting point. We study in detail the central thermodynamic quantity, the free energy surface, and show that a high quality prediction of its temperature and volume dependence is crucial to guarantee an unbiased description of derived materials properties. This turns out to be particularly challenging at high temperatures due to the fact that the numerical/controllable errors propagate in a strongly increasing fashion with temperature. We therefore developed and applied a set of novel approaches going significantly beyond previous studies: 1) A method to efficiently assess the controllable errors in all relevant free energy contributions and to reduce them to a few meV/atom even at the highest temperatures. 2) A hierarchical coarse graining scheme to efficiently determine the anharmonic free energy contribution, which accounts for the atomic interaction beyond the simple analytic harmonic description and which therefore usually represents a formidable computational challenge. 3) A general and intuitive treatment of the free energy contribution due to point defects from which the standard approaches can be easily derived as approximations.

Our methods can be applied to resolve long standing uncertainties about physical mechanisms such as, e.g., the evaluation of the effects eventually leading to the transition from the solid to the liquid phase. One of these decisive problems, which remained unresolved for over 90 years, is the detailed balance of contributions to the heat capacity of a metal before melting. Investigating the example of aluminum in detail, our approach allowed for the first time an accurate quantification of all relevant excitation mechanisms and thus to settle a long standing debate. These findings indicate that the methods developed and applied in this study represent an important step towards the general goal of a materials design solely on the computer.