Calculating free energies of point defects from *ab initio* ☆

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ABSTRACT

The formation and lifetime of point defects is governed by an interplay of kinetics and thermodynamic stability. To evaluate the stability under process conditions, empirical potentials and *ab initio* calculations at $T = 0$ K are often not sufficient. Therefore, various concepts to determine the full temperature dependence of the free energy of point defects with *ab initio* accuracy are reviewed. Examples for the importance of accurately describing defect properties include the stabilization of vacancies by impurities and the non-Arrhenius behaviour of vacancy formation energies due to anharmonic lattice vibrations.

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1. Introduction

Defects have been in the focus of experimental and theoretical research for decades due to their decisive role for materials properties. A comprehensive knowledge of defects' behavior is of particular importance for controlling radiation effects and improving the performance of materials under irradiation, which depends strongly on the evolution of radiation-induced defects [1]. Atoms are displaced by collision cascades, whereby the first "ballistic stage" produces within a few picoseconds a significant number of point defects, mainly Frenkel pairs. These defects evolve during the subsequent long-term "recovery stage" through thermally-activated, diffusion-controlled processes, including migration and recombination, elimination or annihilation, critically influencing the performance and lifetime of irradiated materials.

To understand defect evolution and reveal the relevant mechanisms, calculations and simulations have become a common supplement to experiment. The primary damage production process is typically addressed by molecular dynamics (MD) simulations [2–5], while the recovery stage generally requires simulations going beyond the time scale accessible with MD. To go to large time scales, rate theory [6], kinetic Monte Carlo [7,8], or cluster dynamics [9] are used. Applying these computational tools has enabled the determination of critical guidelines in designing new and better radiation tolerant materials. The predictive power of the simulations is closely linked to the performance of the available interatomic potentials which need to reproduce the fundamental quantum mechanical interactions. The development of

reliable potentials faces specific challenges for radiation damage simulations as an accurate prediction of defect properties, e.g., formation/migration energies or defect-atom bonding energies, requires special care [7].

Due to their approximate nature, semi-empirical interatomic potentials may suffer from providing quantitatively (sometimes even qualitatively) inaccurate defect properties. Therefore, new and advanced parametrizations of interatomic potentials are desirable. However, due to the rather limited number of experimental data on point defect properties, such potentials rely strongly on *ab initio* derived input [7,10–16], usually computed by density functional theory (DFT). Extensive developments of DFT-based techniques—several of which will be in the focus of the present review—have lead to a wide variety of successful applications providing highly-accurate defect formation energies often in exceptional agreement with experimental data [17–22].

Among the various types of defects, point defects (e.g., vacancies or interstitials) are of primary concern in defect evolution [16]. Although the number of point defects produced in the initial ballistic stage is far above the equilibrium concentration, a prerequisite for correctly predicting their evolution is an accurate understanding and description of the intrinsic thermodynamic properties. Modern DFT based techniques can provide in this respect highly accurate input for benchmarking empirical potentials. The thermodynamics of defects becomes also important to understand driving forces behind defect aggregation during the long-term recovery stage.

In the present review we focus on the methodology to accurately determine DFT-based point defect thermodynamics. An essential characteristic of point defects, i.e., 0D defects, is their substantial configurational entropy. This is in obvious contrast to higher dimensional defects such as dislocations (1D) and interfaces

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(2D). Beyond the fundamental interplay between formation energy and configurational entropy that determines the 'usual' equilibrium concentration, a topic of relevance for the recovery stage is the stabilization of point defects, in particular vacancies, by forming complexes/ associates with extrinsic point defects such as hydrogen. These issues will be addressed in Section 2. In Section 3, we formulate and describe techniques to assess entropy contributions beyond the configurational one. A main focus will be on the anharmonic contribution, i.e., phonon-phonon interactions. This contribution requires advanced computational techniques to be accurately captured. As exemplified in Section 4, anharmonic contributions are critical to properly describe the temperature dependent Gibbs energy of vacancy formation and to link experimental data taken at high temperatures with theoretical data commonly computed at $T = 0$ K.

At present a similarly well-developed methodology to address finite temperature contributions to point defect *kinetics*, i.e., migration free energy barriers, is not available. In Section 5 we sketch the basics of calculating defect barriers with *ab initio* and give a short outlook on possible extensions.

2. Configurational thermodynamics of defects

2.1. Defect formation energy

To arrive at an expression for the defect formation energy, we start with the fundamental equation for the change of the system's energy, dE, according to the first law of thermodynamics:

$$dE = \sum_k Y_k \, dX_k$$
$$= T \, dS - P \, dV + \sum_i \mu_i \, dN_i + \sum_d E_f^d \, dN^d + \cdots. \quad (1)$$

Here, Y_k represents a generic intensive, i.e., system size independent, variable and X_k the corresponding conjugate extensive variable, being proportional to the system size. The sum over k runs over all conjugate variable pairs available to the system such as:

- temperature T and entropy S,
- pressure P and volume V,
- chemical potential μ_i and number of atoms N_i of species i,
- defect formation energy E_f^d and number of such defects N^d.

The dots in Eq. (1) indicate the possibility of adding further conjugate pairs. It follows that the defect formation energy can be computed as

$$E_f^d = \left. \frac{\partial E}{\partial N^d} \right|_{S,V,N_i,\ldots}, \quad (2)$$

where all extensive variables except for N^d, i.e., the "invariants", are held fixed. In a typical DFT supercell approach, the derivative in Eq. (2) is replaced with a finite difference:

$$E_f^d = E^{\mathrm{sc}+d}(\{n_i + \Delta n_i\}) - E^{\mathrm{sc}}(\{n_i\}) - \sum_i \Delta n_i \mu_i, \quad (3)$$

where $E^{\mathrm{sc}+d}$ and E^{sc} are the total energies of a supercell with and without the considered defect, Δn_i refers to the number of atoms of type i that have been added to ($\Delta n_i > 0$) or removed from ($\Delta n_i < 0$) the supercell to form the defect and μ_i is the corresponding chemical potential. To determine the required size of the supercell convergence tests are required [15,23]. Particular care has to be taken for magnetic materials, since magneto-elastic coupling effects yield long-range interactions [15]. Modifications of magnetic moments around a point defect (vacancy, interstitial) extend over

many more shells than the relaxation effects in non-magnetic materials [24]. It is also important to note that the magnetic configuration as well as the magnetic order have a strong impact on the defect formation energy [25–27].

2.2. Configurational entropy and defect concentration

In thermodynamic equilibrium, defects with a positive formation energy E_f^d are stabilized by their configurational entropy $S^{\mathrm{conf}} = k_B \ln W$ (k_B = Boltzmann constant), where the number of microstates W for n point defects on N lattice sites is given by

$$W = \frac{(gN)!}{(gN - n)!n!} \approx (gN)^n/n!. \quad (4)$$

Here, g is a geometry factor, which is e.g., $g = 1$ for monovacancies and $g = 6$ for divacancies in fcc lattices. The approximation in Eq. (4) applies for small defect concentrations $c^d = n/N$ and the resulting configurational contribution of the defects to the free energy of the system reads

$$F^{\mathrm{conf}}(c^d, T) = c^d E_f^d - k_B T[c^d - c^d \ln(c^d) + c^d \ln(g)], \quad (5)$$

where the Stirling approximation has been applied. The corresponding defect concentration at thermodynamic equilibrium ($\partial F^{\mathrm{conf}}/\partial c^d \equiv 0$) is given by

$$c_{\mathrm{eq}}^d(T) = g \exp\left(-\frac{E_f^d}{k_B T}\right). \quad (6)$$

For larger defect concentrations the approximation in Eq. (4) may be less appropriate. Assuming non-interacting point defects, it is possible to derive an expression that takes into account the reduced number of defect free sites. For $g = 1$ the configurational free energy then reads

$$F^{\mathrm{conf}}(c^d, T) = c^d E_f^d + k_B T[c^d \ln(c^d) + (1 - c^d) \ln(1 - c^d)], \quad (7)$$

and the concentration

$$c_{\mathrm{eq}}^d(T) = \left[\exp\left(\frac{E_f^d}{k_B T}\right) + 1\right]^{-1}, \quad (8)$$

which follows a Fermi-Dirac distribution that reduces in the dilute limit to the Boltzmann distribution in Eq. (6). Note that large defect concentrations also modify the chemical potentials μ_i of the species forming the material [28], which needs to be self-consistently taken into account in Eq. (3).

2.3. Stabilization of vacancies by other defects

In contrast to the situation in structurally perfect, unary bulk materials, the defect concentration in real materials is inhomogeneous and depends on the local environment. This applies in particular to the situation in radiation damage, where multiple point defects such as vacancies, self-interstitials and impurity interstitials are expected to occur simultaneously. Whenever their interaction has a positive energy (i.e., is attractive), they stabilize each other and may form defect complexes [15,29,30].

An important phenomenon related to this interplay is the so-called superabundant vacancy formation [31], which is observed in various metallic materials and steels. A particularly omnipresent element is hydrogen. Consequently, the role of interstitial H atoms on the formation and concentration of intrinsic defects such as vacancies has been the subject of intensive experimental [32,33] and theoretical [24,34] investigations.

Using the example of hydrogen-vacancy complexes, we discuss in the following the formalism to treat complexes consisting of two