
Chapter 9.

Atomic transport properties

M. Freyss

CEA, DEN, DEC, Centre de Cadarache, France

Abstract

As presented in the first chapter of this book, atomic transport properties govern a large panel of nuclear fuel properties, from its microstructure after fabrication to its behaviour under irradiation: grain growth, oxidation, fission product release, gas bubble nucleation. The modelling of the atomic transport properties is therefore the key to understanding and predicting the material behaviour under irradiation or in storage conditions. In particular, it is noteworthy that many modelling techniques within the so-called multi-scale modelling scheme of materials make use of atomic transport data as input parameters: activation energies of diffusion, diffusion coefficients, diffusion mechanisms, all of which are then required to be known accurately. Modelling approaches that are readily used or which could be used to determine atomic transport properties of nuclear materials are reviewed here. They comprise, on the one hand, static atomistic calculations, in which the migration mechanism is fixed and the corresponding migration energy barrier is calculated, and, on the other hand, molecular dynamics calculations and kinetic Monte-Carlo simulations, for which the time evolution of the system is explicitly calculated.

Introduction

In nuclear materials, atomic transport properties can be a combination of radiation effects (atom collisions) and thermal effects (lattice vibrations), this latter being possibly enhanced by vacancies created by radiation damage in the crystal lattice (radiation enhanced-diffusion). Thermal diffusion usually occurs at high temperature (typically above 1 000 K in nuclear ceramics), which makes the transport processes difficult to model at lower temperatures because of the low probability to see the diffusion event occur in a reasonable simulation time. In this chapter, some methods will be reviewed that

enable one to apprehend atomic transport properties in solids and which are currently used for nuclear materials or which show great potential.

The basic equation to express the thermal contribution to the atomic transport properties (in particular self-diffusion) is the Fick law, giving the atom flux \mathbf{J} in the crystal:

$$\mathbf{J} = -D \cdot \nabla c \quad (1)$$

where c is the atom concentration and D is the diffusion coefficient (assumed isotropic in Equation 1). Diffusion is strongly affected by the microstructure and composition of the material. Atomic transport properties can be strongly dependent on the stoichiometry of the compound, the presence of grain-boundaries or surfaces, the concentration of point defects or impurities, etc. The diffusion equation 1 has to take into account these various effects by additional terms, in particular in the case of materials under irradiation, terms describing the contribution of intragranular and intergranular diffusion, sink efficiency of point defects, bubble nucleation and re-resolution of fission gases, etc. These various effects make the determination (experimental or theoretical) of diffusion coefficients for a given species difficult. For instance, a large dispersion of experimental data exists for atomic self-diffusion coefficients in UO_2 [1-5].

For a given element and a fixed composition (or stoichiometry) of the compound, the temperature-activated diffusion coefficient in Equation 1 is expressed as:

$$D = f \cdot a^2 \cdot \nu \cdot \exp\left(-\frac{\Delta G}{k_B T}\right), \text{ with } \Delta G \text{ the Gibbs free energy (or free enthalpy) associated}$$

with the diffusion, f is a correlation factor accounting for the fact that successive atom jumps can be related to one another, ν the jump frequency, a is a characteristic diffusion length in the crystal depending on the lattice parameter, T the temperature and k_B the Boltzmann constant. The diffusion coefficient D is often found to obey an Arrhenius law:

$$D = D_o \cdot \exp\left(-\frac{\Delta H}{k_B T}\right) \quad (2)$$

in which ΔH is the enthalpy (or the diffusion activation energy $\Delta H = E_a$) associated with the diffusion, D_o the diffusion pre-factor. The activation energy E_a is generally identified as the sum of the migration energy E_m and the defect formation energy, depending on the diffusing element, on the diffusion mechanism and on the nature of the point defects which mediate the diffusion. The temperature-independent pre-factor D_o then depends on the migration and the defect formation entropies ΔS_f and ΔS_m :

$$D_o = f \cdot a^2 \cdot \nu \cdot \exp\left(-\frac{\Delta S_f + \Delta S_m}{k_B}\right) \quad (3)$$

The knowledge of atomic transport events, even of rare events, is required in order to set up a so-called multi-scale modelling scheme for the evolution of the material [6] and to provide physics-based data for nuclear fuel performance codes [7]. The challenge is then, using state-of-the-art modelling techniques, to calculate the diffusion coefficient D directly or determine separately its various contributions: the possible diffusion mechanisms, the corresponding activation energies, the pre-exponential factor D_o .

including its several components (jump frequency, entropy terms, correlation factor). Several modelling approaches exist to reach this goal, based on atomistic first-principles or empirical potential calculations, or Monte Carlo simulations.

Dynamical calculations: Diffusion coefficients

Molecular dynamics (either *ab initio* or classical) and kinetic Monte Carlo simulations are techniques which enable one to simulate the evolution in time of the system and to directly access the diffusion coefficient of a given species in a material.

a. Molecular dynamics

The time evolution of the system is obtained by solving the Newton equation of motion for the all the atoms of the system. The trajectory as a function of time for each particle of the system is obtained. The accuracy of the calculations is determined by the accuracy with which the interaction potentials between the atoms can be described. The interaction potentials can be either calculated using the electronic structure of the system from first-principles calculations (*ab initio* molecular dynamics) or using interatomic empirical potentials (classical molecular dynamic). For more details on classical molecular dynamics, (see Chapter 13). The accuracy chosen will limit the time scale of the simulation: a few picoseconds for *ab initio* molecular dynamics, and a few nanoseconds for classical molecular dynamics. Most of the transport processes involved in the evolution of nuclear materials (point defect or fission product migration) exhibit, however, energy barriers too high to occur within the time scale of *ab initio* simulation. Most of the molecular dynamics studies of nuclear materials, especially actinide compounds, are still performed using empirical potentials.

Using molecular dynamics, atomic transport properties are determined by the analysis of the trajectories of the atoms as a function of time. Thermal vibrations or complex concerted motions of the atoms can, however, make the determination of elementary migration paths difficult. But one can access the coefficient D , which is expressed as the mean square displacement of an atom species:

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \quad (4)$$

By performing simulations at various temperatures, one can plot the evolution of D as a function of the temperature and extract the pre-exponential factor D_0 by a fit to the Arrhenius law equation 2. The activation energy of a particular diffusion mechanism can, however, hardly be extracted from molecular dynamics simulations because of the concerted motion of all the atoms of the system. Generally, the diffusion mechanism is identified in a molecular dynamics simulation and its activation energy is subsequently calculated using a static calculation method, such as the Nudged Elastic Band (NEB) method presented below.

There are several limitations in the use of *ab initio* or classical molecular dynamics for atomic transport properties. *Ab initio* calculations can only reach simulation times of the order of a few picoseconds with a limited number of atoms involved (several hundreds at most), while in classical molecular dynamics calculations, the number of atoms involved can reach billions and the timescale is significantly increased to around 10-100 ns. But in

many cases, it is still not enough to observe diffusion events that are too slow and involve a large energy barrier, like for instance uranium or xenon diffusion in UO_2 . For such processes, either static migration methods have to be used (see below) or accelerated dynamics algorithms.

b. Accelerated dynamics

Accelerated dynamics methods such as temperature-accelerated dynamics simulations [8] introduce a fictitious temperature to the system in order to ease the climbing of potential barriers and thus artificially accelerate the time evolution of the system. The temperature can be raised typically to 3 000 K, the challenge being the conservation of the correct dynamics at the original temperature. Similarly, in hyperdynamics [9] or metadynamics [10] calculations, a bias potential raises the energy in regions other than the transition states between potential basins, enabling the exploration of the potential energy surface and making transitions occur at an accelerated rate without the prior knowledge of the states through which the system may evolve.

Classical molecular dynamics calculations have been used to model various aspects of atomic transport properties of point defects and fission products in nuclear fuel materials. For instance, in the case of UO_2 : defect recombination [11,12], diffusion induced by displacement cascades [13-16], influence of grain boundaries and dislocations [17,18], rare gas diffusion and resolution [19-23], etc.

c. Kinetic Monte Carlo

KMC simulations [24] are another approach to determine the time evolution of a system from which diffusion coefficients may be directly extracted. Its advantage over classical molecular dynamics is that it enables to access larger timescales, but it is based on the prior knowledge of all the various mechanisms by which the system can evolve. It cannot predict a migration mechanism by itself. A list of migration mechanisms and their associated migration barriers are input data of the simulation. These data are often provided by *ab initio* or empirical potential calculations or extracted from experimental data. Kinetic Monte Carlo is based on the calculation of the probabilities of all the possible transitions of the system (see Chapter 17). KMC has only been recently applied to the study of atomic transport properties in nuclear fuels. An example is the calculation of oxygen diffusivity in UO_2 as a function of the stoichiometry [25].

Static calculations: Migration barriers

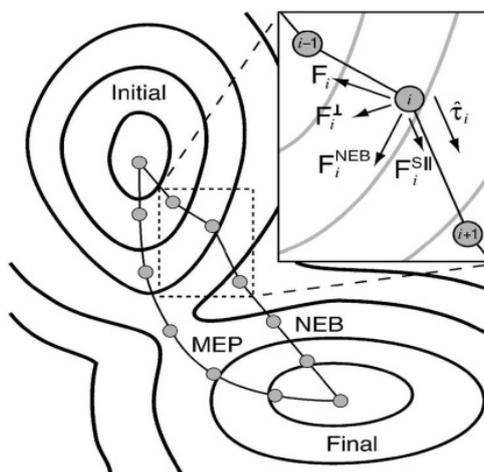
Static calculations are an alternative to dynamical simulations for the study of transport properties in materials. The goal of static migration calculations is to determine the energy barrier that the migrating atom has to overcome in order to hop from one position in the crystal to the next. In this approach, the time evolution of the system does not come into play. The migration energy is determined by the calculation of the energy of the system upon displacement of the migrating atom in the crystal. The challenge for static migration calculations is to find the most favourable migration mechanism, the minimum-energy path (MEP), which is starting from a local energy minimum and leading to another local energy minimum, passing through a saddle point. The energy of the saddle point relative to the local energy minimum is defined as the migration energy E_m . Several such static methods have been developed, among them the Nudged Elastic Band (NEB) method [26],

the string method [27,28], the dimer method [29], the Activation-Relaxation Technique (ART) [30-33].

a. The Nudged Elastic Band (NEB) and the string methods

These methods are used to find reaction pathways when both the initial and final states are known. An initial migration path is interpolated and discretised into a set of images between the known initial and final states. The total energy of the images, corresponding to intermediary configuration of the migrating atom along the migration path, is then minimised. The NEB method is based on a spring interaction between adjacent images which is added to ensure continuity of the path, thus mimicking an elastic band. The forces acting on each image that should be minimised are the normal component of the potential force and the tangential component of the spring force (see Figure 1). In the string method, an elastic chain of configurations joining the initial and final states is progressively driven to the minimum energy path using an iterative procedure consisting of two steps: (1) evolution step: the images are moved following the atomic forces, (2) reparametrisation step: the images are equally redistributed along the string. In both NEB and string methods, the atomic positions of the system are optimised at each step of the migration to ensure that the minimum energy path is found. The climbing-image method [33] is an improvement of these methods to make one of the images correspond to the saddle point of the migration path for a more accurate determination of the energy barrier. The drawback of the NEB and the string methods is that the final state of the migration has to be known: one has to explore many migration mechanisms in order to find the diffusion process with the lowest migration barrier that will be thus the most probable to occur.

Figure 1. Two components making up the nudged elastic band force F_i^{NEB} : the spring force $F_i^{S||}$ along the tangent and the perpendicular force F_i^{\perp} due to the potential [35]



b. The dimer method and Activation-Relaxation Technique (ART)

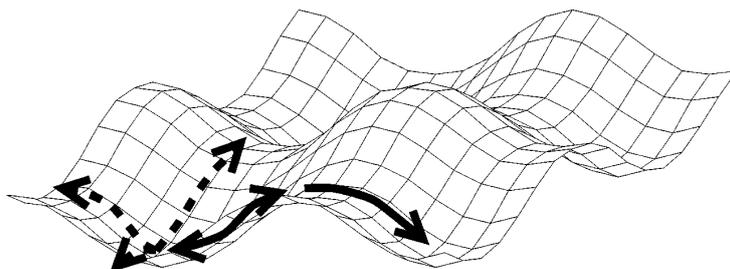
Contrary to the NEB or the string methods, these methods require the knowledge of neither the final state of migration nor the saddle points: it allows the system to evolve following well-defined paths between local energy minima, starting from the knowledge of only one local minimum. The dimer method [27,28] is used to find saddle points by defining two replicas (dimer) of the system with slightly displaced coordinates in order to

explore the curvature of the potential energy surface. The ART method [30-33] proceeds in two steps starting from a local minimum:

- activation: the configuration is moved from a local minimum to a nearby local saddle point;
- relaxation: the system is pushed over the saddle point and relaxed to a new minimum.

The first step is achieved by defining a modified force field in which the saddle is a minimum. The dimer and the ART methods allow one to jump over much higher energy barriers than allowed by standard molecular dynamic techniques and can thus predict migration mechanisms and activation energies in complex local atomic arrangements or in disordered materials. For nuclear materials such as UO_2 , such methods should be, however, used with caution because of the large difference between oxygen and uranium migration barrier: only migration events involving oxygen ions would most probably be obtained.

Figure 2. Illustration of the activation and relaxation steps in ART for a two-dimensional energy landscape [30]



From each energy minimum, the system can reach several saddle points. The down-pointing arrows from the saddle point indicate the directions of the force toward a minimum energy. The full line arrows show the path for a single event.

In the static migration approaches, the interatomic interactions can be calculated from either first-principles or empirical potential calculations. ART has been recently applied to point defects in metals [36], silicon carbide [37], amorphous silica [31]. For nuclear fuel applications, the NEB method has been mostly used so far in order to determine migration mechanisms and to calculate migration energies of point defects and fission products. For instance, in the case of UO_2 , using the first-principles DFT+U method, the migration of oxygen [25,38] uranium [39,40] and xenon [39] atoms has been studied. These studies follow many previous works making use of standard DFT [41,42], which is unfortunately not appropriate for a correct description of the electronic properties of UO_2 (see Chapter 12). Using empirical potentials, pioneering works in the eighties and early nineties were already able to identify migration mechanisms of point defects [43] and xenon atoms [44,45] in UO_2 with static migration calculations. They were later completed by the use of several empirical pair-potentials for the study of transport properties of point defects [46], dislocations [47], fission gases and helium [48] in UO_2 .

Vibrational properties: Pre-exponential factor

a. Entropic contributions to the pre-exponential factor

Atomic transport properties can be apprehended by the calculation of the vibrational properties of the system. The diffusion prefactor D_0 is indeed expressed as a function of migration and defect formation entropy ΔS_f and ΔS_m (Equation 3 – in which the electronic entropy contribution is generally neglected). The formation entropy is related to the phase-space volume accessible to the defects and involves configurational and vibrational contributions: $\Delta S_f = \Delta S_{f,conf} + \Delta S_{f,vib}$. The configurational contribution is purely geometric and depends on the number of configurations Ω that the diffusing defect can take in the lattice: $\Delta S_{f,conf} = k_B \ln \Omega$. The vibrational contribution $\Delta S_{f,vib}$ is the difference between the vibrational entropy of the system containing the defect and the vibrational entropy of the perfect system without defect. In the harmonic approximation, it can be expressed as a function of the phonon frequencies ν_i^0 of the perfect system (containing N atoms) and the phonon frequencies ν_i' of the defective system, which can be calculated using first-principles or empirical potential calculations:

$$\Delta S_{f,vib} = k_B \ln \frac{\prod_{i=1}^{3N} \nu_i^0}{\prod_{i=1}^{3N} \nu_i'} \quad (5)$$

The migration entropy ΔS_m is defined as the difference in entropy between the system in which the diffusing atom is at a local stable position (local minima 0) and at a saddle-point position (or transition state TS): $\Delta S_m = S_{vib}^{TS} - S_{vib}^0$. The migration entropy can again be calculated from the phonon spectra of the system. In the harmonic approximation ΔS_m can be expressed, similarly to the formation entropy, as a function of the phonon frequencies ν of the system at the equilibrium and transition states:

$$\Delta S_m = k_B \ln \frac{\prod_{i=1}^{3N} \nu_i^0}{\prod_{i=1}^{3N-1} \nu_i^{TS}} \quad (6)$$

The denominator specifically excludes the frequency in the direction of the motion corresponding to an unstable mode at the transition state.

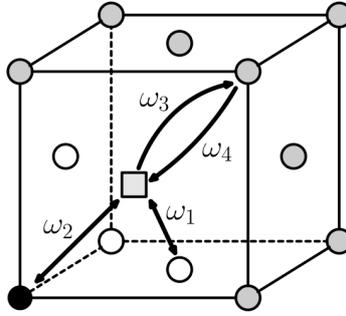
b. Five-frequency model for impurity diffusion

The diffusion pre-exponential factor for impurities can also be determined using a model describing the diffusion mechanisms of the impurity (in dilute concentration) called the five-frequency model. Assuming that the impurity jumps are affected by the presence of vacancies only in the immediate vicinity, A.D Le Claire and A.B. Lidiard [49] expressed the diffusion coefficient D_2 of an impurity in a face-centered cubic crystal in terms of five jump frequencies ν and of the self-diffusion coefficient of the pure host element D_0 :

$$\frac{D_2}{D_0} = \frac{f_2}{f_0} \frac{w_4}{w_0} \frac{w_1}{w_3} \frac{w_2}{w_1} \quad (7)$$

where w are the atom jump frequencies, as illustrated in Figure 3; w_0 is the host atom jump frequency in the absence of the impurity, w_1 is the jump frequency for a host atom nearest neighbour to the impurity, w_2 is the impurity atom jump frequency, w_3 is the host atom jump frequency whose jump dissociate the impurity and the vacancy, w_4 is the host atom jump frequency which associates the impurity and the vacancy (reverse of jump w_3). The impurity diffusion correlation factor f_2 can be expressed as a function of the probability of the impurity atom to jump back to its previous position and the jump frequencies [50,51]. Thus, the determination of the diffusion coefficient of the impurity mostly resides in the calculation of the various jump frequencies w .

Figure 3. Illustration of the atom jump frequencies involving the impurity (black circle) and the vacancy (grey square), as defined in the five-frequency model



Based on transition state theory (TST), the jump frequencies can be expressed as: $w = w^* e^{-\frac{\Delta H_m}{k_B T}}$, where ΔH_m is the change in enthalpy of the system between the states in which the diffusing atom is in its initial equilibrium state and at the saddle point of the diffusion path (transition state). This migration barrier can be calculated by static migration calculations as presented in this chapter (the NEB method for instance). w^* is the effective frequency defined by G.H. Vineyard [52] as a function of the vibrational frequencies in the initial equilibrium state ν_i^0 and in the transition state ν_i^{TS} of a system with N atoms and one vacancy:

$$w^* = \frac{\prod_{i=1}^{3N-3} \nu_i^0}{\prod_{i=1}^{3N-4} \nu_i^{TS}} \quad (8)$$

The vibration frequencies ν_i^0 and ν_i^{TS} can be determined by the explicit calculations of the phonon spectrum of the impurity at the equilibrium state and transition state. This can be achieved using first-principles calculations (usually in the harmonic or quasi-harmonic approximations) or empirical potential calculations.

Examples of diffusion prefactor calculations using first-principles methods associated to the determination of the entropic contributions or to the five-frequency model exist for

SiC [53] and metallic alloys [54], among others. Applications to UO_2 are still hampered by the computational cost of phonon spectrum calculations for defect systems.

Conclusions and future challenges

The modelling of atomic transport properties in nuclear fuel materials has much benefited from the increase in computer resources available and from the recent progress made in the coupling of atomistic methods (DFT, empirical potential, kMC, etc). Atomic transport is a key phenomenon in the multi-scale modelling scheme of nuclear fuels.

One of the challenges for the future consists in tightening even more the links between the modelling techniques at the atomic scale and the mesoscale, in particular for fission gas transport. The study of radiation damage and atomic transport properties in nuclear fuels would also benefit from efficient accelerated dynamics schemes to access fuel evolution during longer timescale and the application of *ab initio* molecular dynamics to actinide compounds.

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