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Following atomistic kinetics on experimental timescales with the kinetic Activation–Relaxation Technique

Normand Mousseau [a,b,*], Laurent Karim Béland [e], Peter Brommer [c], Fedwa El-Mellouhi [f,g], Jean-François Joly [d], Gawonou Kokou N'Tsouaglo [a], Oscar Restrepo [a,g], Mickaël Trochet [a]

[a] Département de physique, Université de Montréal, Case postale 6128, succursale centre-ville, Montreal, QC H3C 3J7, Canada
[b] Theoretical Physics, Utrecht University, Utrecht, The Netherlands
[c] Centre for Predictive Modelling, School of Engineering, University of Warwick, Library Road, Coventry CV4 7AL, UK
[d] Carleton University, Ottawa, ON, Canada
[e] Materials Science and Technology Division, Oak Ridge National Laboratory, TN, USA
[f] Qatar Environment and Energy Research Institute, Doha, Qatar
[g] Texas A&M University at Qatar, Doha, Qatar

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ABSTRACT

The properties of materials, even at the atomic level, evolve on macroscopic time scales. Following this evolution through simulation has been a challenge for many years. For lattice-based activated diffusion, kinetic Monte Carlo has turned out to be an almost perfect solution. Various accelerated molecular dynamical schemes, for their part, have allowed the study on long time scale of relatively simple systems. There is still a need, however, for methods able to handle complex materials such as alloys and disordered systems. Here, we review the kinetic Activation–Relaxation Technique (k-ART), one of a handful of off-lattice kinetic Monte Carlo methods, with on-the-fly cataloging, that have been proposed in the last few years.

1. Introduction

Computational materials science covers a wide range of time and length scales: from the electronic motion to crack propagation and aging. Among the challenges that this discipline faces is the need to cover multiple scales in a self-coherent fashion in order to relate with experiments and real-life phenomena. In spite of considerable efforts that have spanned decades, no complete answer to this challenge exists. Nevertheless, progress takes place and partial solutions are being proposed and applied, not necessarily to generic problems, but at least to specific classes of technologically-relevant materials. Irrespective of these unwelcome restrictions, these developments constantly open up new areas of study to the field.

Here, we are concerned with bridging the time gap between simulations and experiments while preserving a detailed description at the atomic level. This concern is not new. Over the past four decades, a number of groups have proposed methods to achieve this goal [1–7]. In this review, we focus on a recently proposed algorithm, the kinetic Activation–Relaxation Technique (k-ART) [8,9], a method that bridges the time domain reaching, at experimentally-relevant temperatures, a second and event more. k-ART describes the atomic motions as particles diffuse and affect microscopic and macroscopic properties of complex materials dominated by activated processes. More precisely, k-ART is an off-lattice kinetic Monte Carlo method with on-the-fly cataloging capabilities. First proposed in Ref. [8], it has since been applied to a number of systems – including implanted crystalline silicon, amorphous silicon, crystalline iron and, more recently, alloys, showing a rich versatility and providing important insights by following the atomistic off-lattice motion of these complex systems over a time scale of up to one second and more [9–12]. In this review, we present an overview of k-ART (Section 2), that will allow the reader to gain a general understanding of the method, a review of recent applications (Section 3 and a more detailed description of our implementation (Section 4).

Of course, a number of other accelerated methods have been put forward over the years, many if which are described elsewhere in this special issue, and we briefly compare them to k-ART in Section 5. We will show, in particular, that k-ART is uniquely suited for the simulation of a large number of complex systems where

* Corresponding author at: Département de physique, Université de Montréal, Case postale 6128, succursale centre-ville, Montreal, QC H3C 3J7, Canada.
E-mail address: normand.mousseau@umontreal.ca (N. Mousseau).

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atoms are not confined to crystalline lattice position and where elastic deformations are important.

2. An overview of k-ART

Kinetic ART is a stochastic event-based kinetic algorithm. This means that its time scale is set by the nature of the local energy landscape and not by the integration of the equations of motion as in molecular dynamics. When the right conditions are met, the trajectory produced with this method is as valid and physical as with molecular dynamics. These conditions are well-defined by the transition state theory (TST), developed independently by Eyring [13] and Evans and Polanyi [14] (see Ref. [15] for a historical perspective). Fig. 1 presents the flowchart for this algorithm, which is detailed in the rest of this section.

2.1. The fundamentals of kinetic Monte Carlo

Here, we are concerned with the time evolution of a system characterized by relatively deep local metastable states, i.e. states isolated from others by energy barriers that are high with respect to the temperature. In this case, the time evolution is controlled by rare barrier crossings that bring the system from a well-defined local minimum into a new one. This rare-event process ensures that hops from local minimum to local minimum are completely uncorrelated so that the escape event selected at a time t_n is perfectly independent from that at time t_{n-1} (see Fig. 2). It also ensures that no two hops take place at exactly the same time, so that events can be uniquely ordered in time. In this case, the dynamical role of phonons – or thermal vibrations – becomes limited to decorrelating the hops and to provide a rare boost through thermal fluctuations. Thermal vibrations allow therefore the system to gain sufficient energy in a given direction and to reach a transition state leading to a new minimum. When these criteria are met, the transition state theory establishes how one can go to compute the escape rates from a local minimum (see, for example, Voter et al. [15]). With these rates at hand, as described below, it is then possible to generate physically-based kinetic trajectories that are fully described by minimum-energy configurations along the way and the escape rates towards neighboring states.

The basic idea behind kinetic Monte Carlo (KMC), introduced by Bortz et al. [16] and first applied to materials by Voter [17], is that when a system is trapped into an energy-minimum separated by

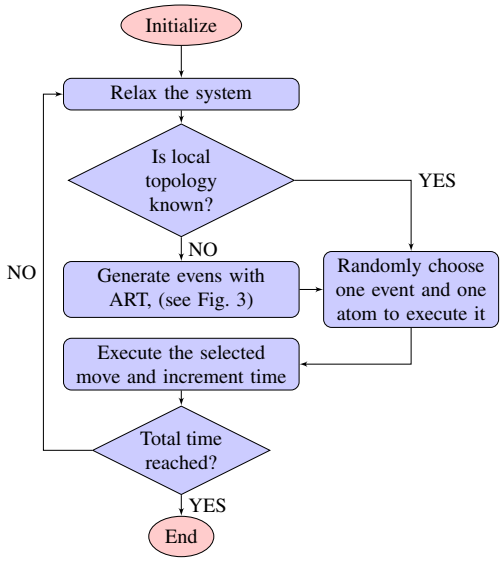

Fig. 1. Flowchart of the implementation of k-ART structure.

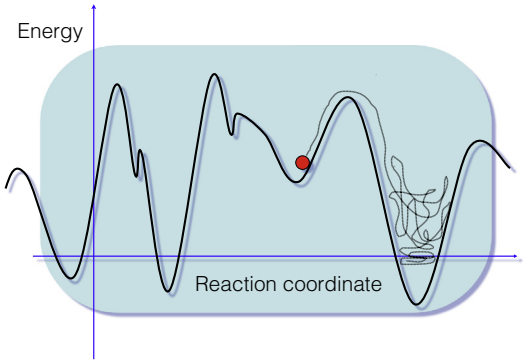

Fig. 2. Schematic representation of the energy landscape surrounding a deep local minimum. The thin black line represents a trajectory through the landscape. Since the barriers leading out of the local minimum in the center are high with respect to the temperature, the system spends a long time in this basin, and has lost memory of its past states by the time it manages to escape. It is therefore possible to fully characterize this state by the minimum-energy configuration, at the bottom of this well, and the curvature around this minimum.

large enough barriers with respect to the temperature, all memory from its previous states is forgotten before it leaves for a new states. This decorrelation is fully justified by the fundamentally chaotic nature of (deterministic) dynamical trajectories (see [18], for example). In this case, it is possible to simply consider that the pathway is constructed of uncorrelated steps each determined at random from a set of events $\{j\}$ associated to a minimum i, each defined by its own rate, $R_{i\to j}$.

The time evolution through those internal stochastic processes, is simply driven by the master equation

$$\frac{\partial P_i(t)}{\partial t} = \sum_j \left(P_j(t)R_{j\to i} - P_i(t)R_{i\to j}\right), \tag{1}$$

which gives us the probability P_i of finding the system in the minimum i at time t. Here, j runs over all states except i.

Since the probability that any event takes place is considered random, the escape rate r_e^i from the local minimum is simply given by the sum of the rates

$$r_e^i = \sum_j R_{i\to j}, \tag{2}$$

with the first-passage escape time out of the minimum taken from a Poisson distribution characterized by this escape rate,

$$t_e = -\frac{\ln \mu}{r_e^i}, \tag{3}$$

where μ is a random number taken from $[0,1]$ at which point an event j is produced with a probability given by its relative rate:

$$\mathcal{P}_{i\to j} = \frac{R_{i\to j}}{r_e^i}. \tag{4}$$

Algorithmically, KMC consists therefore only of three steps:

1. From a given configuration, identify all escape events and their associated rate.
2. Compute the first-passage escape time (Eq. (3)).
3. Select an event at random with the proper probability (Eq. (4)) and move the system accordingly.

Those simple three steps allow us to solve equation (Eq. (1)) through a stochastic approach. The elegance of this method lies in its simplicity but also in the fact that, contrary to most Monte Carlo algorithms, selected events are always accepted.

For lattice-based problems with short-range interactions, the implementation of KMC is straightforward as rates are readily defined at the root of the model itself.