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Examining Saddle Point Searches in the Context of Off-Lattice Kinetic Monte Carlo

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Abstract. In calculating the time evolution of an atomic system on diffusive timescales, off-lattice kinetic Monte Carlo (OLKMC) can sometimes be used to overcome the limitations of Molecular Dynamics. OLKMC relies on the harmonic approximation to Transition State Theory, in which the rate of rare transitions from one energy minimum to a neighboring minimum scales exponentially with an energy barrier on the potential energy surface. This requires locating the index-1 saddle point, commonly referred to as a transition state, that separates two neighboring energy minima. In modeling the evolution of an atomic system, it is desirable to find all the relevant transitions surrounding the current minimum. Due to the large number of minima on the potential energy surface, exhaustively searching the landscape for these saddle points is a challenging task. In examining the particular case of isolated Lennard-Jones clusters of around 50 particles, we observe very slow convergence of the total number of saddle points found as a function of successful searches. We seek to understand this behavior by modeling the distribution of successful searches and sampling this distribution to create a stochastic process that mimics this behavior. Finally, we will discuss an improvement to a rejection scheme for OLKMC where we terminate searches that appear to be failing early in the search process.

AMS subject classifications: 65C05
Key words: Off-lattice kinetic Monte Carlo, energy landscape, saddle point search, dimer method, Lennard-Jones clusters.

1 Introduction

Simulating the time evolution of an atomic scale system in which a chemical reaction or diffusion occurs is an essential task in the study of condensed matter physics and material science. While molecular dynamics (MD) is often the preferred approach, it suffers

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from a severe timescale limitation due to the need to integrate the classical equations of motion for all the particles in the system using a time step on the order of a femtosecond. This restricts the timescale on which MD can simulate events to mere nanoseconds, while diffusion and chemical reactions can take much longer. Off-lattice kinetic Monte Carlo (OLKMC), first introduced by Henkelman and Jónsson [4], is aimed at overcoming this limitation. As explained further below, the essential challenge with OLKMC lies in repeatedly building catalogs of saddle points/transition states. In this paper, we explore several related aspects of these saddle point searches.

OLKMC relies on the observation that the system will spend the majority of its time oscillating within the N_p-particle configuration space about a local minimum of the potential energy function, with rare transitions from one basin of attraction to another. The energy landscape typically features an enormous number of local minima, each of which is connected to a large number of neighboring minima that can be reached by crossing a single saddle point. In view of this, OLKMC seeks to replace the Newtonian dynamics of MD with a Markov chain model, with dynamics given by jumps between discrete states, represented by the local minima. The rates for these transition processes are estimated using the harmonic approximation to Transition State Theory (TST) [1], also known as Vineyard Theory [13]:

$$R_{ij} = K \exp^{-\Delta\phi_{ij}/k_B T}, \tag{1.1}$$

where $\Delta\phi_{ij}$ is the energy barrier that must be overcome in moving from basin i to a neighboring basin j, k_B is Boltzmann's constant, T is the system temperature, and K is a prefactor which we will take to be constant for the purpose of our discussion.

Determining the set of accessible states and the corresponding rates at each time step requires searching the potential energy surface (PES) for index-1 saddle points, where the gradient of the potential is zero and all but one of the principal curvatures is positive. The energy barrier is the difference between the saddle point (*transition state*) energy and the minimum energy, also known as the *binding state* energy:

$$\Delta\phi_{ij} = \phi(X_{ij}) - \phi(X_i), \tag{1.2}$$

where X_i is the current minimum configuration and X_{ij} is an index-1 saddle configuration. Ideally—for the method to yield a faithful representation of the dynamics—one would need to build an exhaustive catalog of *connected* index-1 saddle points at each discrete time step, where "connected" indicates that the current binding site can be reached from the saddle point/transition state by a path that is strictly descending. The difficulty in building such a catalog stems from the large number of individual searches that must be performed in order to explore the PES.

For the most part, we focus on two issues associated with OLKMC. The first issue is relevant to all OLKMC methods and concerns the *global search* for all of the connected saddle points as outlined above, while the second issue deals with an inefficiency in doing a certain type of *local search* to be described below. The issue associated with the global search is illustrated by considering what we will refer to as the *accumulation plot*,