Commun. Comput. Phys.
doi: 10.4208/cicp.130410.031210a

Vol. **10**, No. 4, pp. 920-939
October 2011

A Kinetic Monte Carlo Approach for Self-Diffusion of Pt Atom Clusters on a Pt(111) Surface

R. Deák[1,2], Z. Néda[1,*] and P. B. Barna[3]

[1] *Department of Theoretical and Computational Physics, Babeş-Bolyai University, RO-400084, Cluj-Napoca, Romania.*
[2] *Department of Materials Physics, Eötvös Loránd University, H-1117, Budapest, Hungary.*
[3] *KFKI-MFA, Research Institute for Technical Physics and Materials Science, H-1525, Budapest, Hungary.*

Received 13 April 2010; Accepted (in revised version) 3 December 2010

Communicated by Leonardo Golubovic

Available online 13 June 2011

Abstract. A lattice Kinetic Monte Carlo (KMC) approach is considered to study the statistical properties of the diffusion of Pt atom clusters on a Pt(111) surface. The interatomic potential experienced by the diffusing atoms is calculated by the embedded atom method and the hopping barrier for the allowed atomic movements are calculated using the Nudged Elastic Band method. The diffusion coefficient is computed for various cluster sizes and system temperatures. The obtained results are in agreement with the ones obtained in previous experimental and theoretical works. A simple scaling argument is proposed for the size dependence of the diffusion coefficient's prefactor. A detailed statistical analysis of the event by event KMC dynamics reveals two important and co-existing mechanisms for the diffusion of the cluster's center of mass. At low temperatures (below $T=400$K) the dominating mechanism responsible for the displacement of the cluster's center of mass is the periphery (or edge) diffusion of the atoms. At high temperatures (above $T=800$K) the dissociation and recombination of the clusters becomes more and more important.

PACS: 05.10.-a, 68.35.Fx, 68.43.Jk
Key words: Kinetic Monte Carlo methods, surface diffusion, diffusion coefficient.

1 Introduction

Understanding surface diffusion of single adatoms and small adatom clusters is an important step for realistic modeling of various phenomena related to thin film growth: island nucleation, island coalescence and Ostwald ripening [1]. Over the years experimental techniques, like scanning tunneling microscopy (STM) [2,3] and Field Ion Microscopy

*Corresponding author. *Email address:* zneda@phys.ubbcluj.ro (Z. Néda)

(FIM) [4–7] was used to obtain precious insight into this phenomena. Experimental observations were completed by several theoretical methods like static calculations [8–10], molecular dynamics (MD) [11,12] and Monte Carlo methods (MC) [13,14]. In the present work a Kinetic Monte Carlo (KMC) approach is considered to study the diffusion coefficient of single Pt atoms and clusters on Pt(111) surface.

It is a well-known fact that MC simulations are less accurate approximation to reality than the nowadays fashionable *ab*-initio Molecular Dynamics methods (for a review see [15]). The advantage of the *ab*-initio methods is that they do not rely on phenomenological interaction potentials but calculate them from first-principles. *Ab*-inito MD simulations provide an accurate description of inter-atomic interactions, but naturally there is price to pay for this. The price is the extremely long computational time. Therefore *ab*-initio methods are restricted to relatively small systems and short simulation times. The very short time-scale which is manageable on modern supercomputers (of the order of nano-seconds) makes these methods inappropriate for studying the diffusion coefficient of the surface diffusion. In contrast to MD methods, in KMC simulations several processes are taken into account in a phenomenological manner, many times without a microscopic foundation. The interaction potentials governing the dynamics of the atoms and consecutively the values of energy barriers for the particle moves are either heuristic ones or approximated from Density Functional Theory (DFT) calculations [16]. MC simulations offer, however, a great advantage (for a review see [17]): it is fast and one can study thus larger systems and much longer time-scales. Due to these advantages the method is more adaptable for moderate computational resources than MD methods. With KMC methods a quite reasonable number of atoms can be studied on cheap PC type computers. MD methods and MC methods are complementing thus each other. Parallel with developing fast and realistic MD methods, making the KMC simulations more realistic is also an important task. KMC simulations are nowadays targeting structures on mesoscopic scale or complex phenomena that has characteristic time-scale of the order of seconds or larger. Since the characteristic time-scale for the diffusion of adatom clusters on a crystalline surface is much larger than the time-scales manageable by MD methods we have chosen to consider an up to date KMC method.

The present paper is structured as follows. In Section 2 we describe briefly the main elements of the KMC method and how the method is implemented for the specific problem considered in the present work. In Section 3 we discuss some theoretical arguments regarding the diffusion coefficient and its variation as a function of temperature and cluster size. KMC simulation results are presented and discussed in Section 4. Section 5 is devoted to general conclusions.

2 The KMC approach and computational details

2.1 The KMC method, a brief review

Kinetic (sometimes labeled as resident-time, or BKL-type) Monte Carlo methods [18] are appropriate for simulating those dynamical phenomena where several processes with