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研究課題名（和文）ナノ構造形成過程の解明に向けた動的モンテカルロ法

研究課題名（英文）Development of a direct kinetic Monte Carlo method for the investigation of nanostructure formation processes

研究代表者

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研究成果の概要（和文）：GRRMとDFTBをつなぐためのプログラムを完成させた。DFTにくらべDFTB3は1000倍高速なので、Kinetic Monte carloをon-the-flyで組み合わせることができた。
開発したflyKMCは、鉄粒子上での炭素の移動速度に関して、DFTBポテンシャルを用いた別の量子分子動力学と同程度のオーダーでよい一致を示した。

研究成果の概要（英文）：We have successfully connected the global reaction route mapping (GRRM) method for use with the density-functional tight-binding (DFTB) quantum chemical potential. Since DFTB is 3 orders of magnitude faster than conventional DFT methods, it became possible to use the GRRM-DFTB combination in on-the-fly kinetic Monte Carlo simulations. "flyKMC" achieved good agreement with the 1st order kinetics of carbon atom migration on an iron nanoparticle observed during independent quantum chemical molecular dynamics simulations using the DFTB potential.

研究分野：　物理化学

キーワード：　kinetic Monte Carlo　nanostructure formation　extended timescale　molecular dynamics

１．研究開始当初の背景

Two of the most common methods for simulating chemical equilibria and non-equilibrium processes are molecular dynamics (MD), a purely deterministic method based on the classical laws of motion, and the Monte Carlo method (MC), a method which samples the local potential energy surface (PES) on a stochastic basis. Both MC and MD can predict the time-averaged properties of atomic and molecular ensembles. The accuracy of these properties in both cases is limited by how efficiently the electronic energy of the system can be calculated. MD can also predict the time evolution of atomic ensembles, but is limited by how efficiently the interatomic forces can be calculated at each simulation step. This limits the timescale of these methods, and hence what chemical processes they can meaningfully simulate. Hybrid MD/MC methods and force bias MC methods also have this limitation. Molecular dynamics is restricted further by the requirement that the time integration step must be sufficiently small so that nuclear motion over the PES is integrated smoothly, thus avoiding unrealistic dynamics. This is particularly the case for chemically reactive systems. A commonly quoted heuristic is that the time step must be (at most) 50% of the highest frequency vibrational mode present in the system. There have been several attempts aimed at overcoming this “time scale problem”. Notable advances include force biased and time-stamped force biased MC methods, parallel replica dynamics, umbrella sampling, hyperdynamics, temperature-accelerated dynamics and bond-boosting methods, and collective variable-driven hyperdynamics (CVHD).

２．研究の目的

Amongst the most versatile solutions to the timescale problem, and in particular the problem of rare events, are on-the-fly kinetic MC methods. The key limitation of KMC in this respect is that a complete set of state-to-state transitions and their associated rate constants must be known in advance. This means that traditional KMC is incapable of simulating emergent phenomena, such as self-assembly. The goal of our project was to create a methodology that is computationally feasible as an on-the-fly KMC method.

３．研究の方法

On-the-fly KMC, on the other hand, determines state-to-state transitions based on the nature of the local PES around a particular local minimum, at each state of the system. While on-the-fly KMC removes the need for an *a priori* move-table, it requires a method of finding all local transition states (TSs). This in itself is a tremendous task but manageable using our new combination of the global reaction route mapping (GRRM) method with the density-functional tight-binding (DFTB) quantum chemical potential (GRRM-DFTB).

４．研究成果

Initially GRRM is used to find all transitions states TS_i^j around an equilibrium point EQ_i. Activation barriers ΔE_i^j are used to calculate rate constants k_i^j on the basis of 1st order kinetics. TS_i^m is selected with a probability proportional to the rate constant k_i^m and the total sum of the rate constants k_{tot}. A time step is calculated using equation (5) TS_i^m is used to find the next EQ, EQ_{i+1}^m *via* the IRC between the two stationary points.

As archetypical example, we applied our flyKMC method to the proton transfer in malonaldehyde, since the reactive PES for this process has been studied extensively. We calculated the intramolecular proton transfer in malonaldehyde, calculated using DFTB3/3ob-3-1, M06-2X/aug-cc-pVTZ and MP2/aug-cc-PVTZ. Local minima are left and right, and the proton transfer TS is centre.

Constant temperature (NVT) DFTB3/MD simulations were used to benchmark GRRM-KMC results for intramolecular proton transfer in malonaldehyde. The 3rd-order correction in DFTB3 (term 4, equation (6)), in conjunction with the 3ob parameter sets,[51-54] enables an accurate treatment of hydrogen bonding,[53] which is crucial in the context of intramolecular proton transfer. These DFTB3/MD simulations employed an initial temperature of 298 K. The velocity Verlet algorithm[55] was used to propagate the classical equations of motion, using a time step of 0.1 fs. This timestep is sufficiently small to ensure an accurate description of proton

transfer. Nuclear temperature was maintained at 298 K using a Nosé-Hoover chain thermostat (chain length 3)[56,57] coupled to the degrees of freedom of the system. To ensure reliable statistical sampling, 50 independent trajectories were calculated. Each trajectory began with a 10 ps period of equilibration, before proton transfer was analysed over a subsequent period of 290 ps. This resulted in a total of 1653 proton transfer events being observed.

A comparison between proton transfer frequencies as a function of time, calculated using NVT MD and GRRM-KMC is made in Figure 3. Below 1 ps, an anomalously high transition frequency is observed in Figure 3(a), consistent with previous reports. This is due to the presence of re-crossing events in the DFTB3/MD simulation, and results in a non-exponential decay in the transition frequency at short timescales. These results demonstrate that re-crossing events can be predicted in malonaldehyde using MD in the absence of quantum effects (viz. barrier vanishing and proton tunnelling). By contrast, the decay in transition frequency shown in Figure 3(a) for the GRRM-KMC simulations lacks this non-exponential character at short timescales. These results reflect the fact that deterministic MD can describe re-crossing in malonaldehyde proton transfer (albeit here without describing quantum effects such as proton tunnelling), since the dynamics are propagated directly on the molecular PES. However, GRRM-KMC (and KMC in general) assumes ergodicity; i.e. the time interval separating each state-to-state transition is sufficiently large to enable the molecule to equilibrate between each proton transfer event. Some discrepancy between KMC and MD descriptions of proton transfer kinetics should naturally be anticipated for very fast transitions.

Normalised frequencies of intramolecular proton transfer in malonaldehyde at 298 K, predicted using NVT MD (□) and GRRM-KMC (×): (a) includes all transfer events, including re-crossings faster than 1 ps; (b) excludes transitions faster than 1 ps. Both MD and KMC simulations are performed using the DFTB3/3ob-3-1 method. MD simulations predict a non-exponential decay in transition frequency for transitions < 2 ps. Error bars on MD data points show 1 standard deviation (negative error bars omitted due to logarithmic scale).

We were able to corroborate this; by removing the fast re-crossing events (all transitions faster than 1 ps) a much closer alignment between NVT MD and GRRM-KMC transition distributions is observed. For longer timescale transitions (i.e. > 1 ps), both Figure 3(a) and (b) show much closer agreement between NVT MD and GRRM-KMC transition frequency distributions. The decay in transition frequency are in near perfect agreement here for the two methods.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計 7 件）

1. *Y. Wang, W. Song, M. Jiao, Z. Wu, S. Irle, Importance of Oxygen in Single-Walled Carbon Nanotube Growth: Insights from QM/MD Simulations, Carbon, in press (2017). DOI: 10.1016/j.carbon.2017.06.005*、**査読有**
2. H.-J. Qian, J. Jakowski, G. Eres, **S. Irle,** *Quantum Chemical Molecular Dynamics Simulation of Carbon Nanotube-Graphene Welding,* Molecular Simulation (Special issue on the "The 4th International Conference on Molecular Simulation"), DOI: 10.1080/08927022.2017.1328555、**査読有**
3. Y. Wang, H. Jian, Z. Wu, **S. Irle**, *"QM/MD Simulations on Graphene Hydrogenation/Deuteration: C_xH/D Formation Mechanism and Isotope Effect,* J. Phys. Chem. C **121**(15),

8480-8489 (2017). DOI: 10.1021/acs.jpcc.7b01662、査読有

4. J. Wang, Y.-Y. Zhao, P.-H. Lee, **S. Irle,** *Er^{3+} Photoluminescence in $Er_2@C_{82}$ and $Er_2C_2@C_{82}$ Metallofullerenes Elucidated by Density Functional Theory,* Inorg. Chem., ASAP paper (2017). DOI: 10.1021/acs.inorgchem.7b00695、査読有

5. C. A. Eveleens, Y. Hijikata, **S. Irle,** A. J. Page, *Chirality-Selective Carbon Nanotube Etching with Ammonia: A Quantum Chemical Investigation,* J. Phys. Chem. C **120**(35), 19862-19870 (2016). Received: July 13, 2016, published online: August 10, 2016, publication date: August 10, 2016. DOI: 10.1021/acs.jpcc.6b06997、査読有

6. A. J. Page, I. Mitchell, H.-B. Li, M.-G. Jiao, Y. Wang, **S. Irle**, K. Morokuma, *Spanning the "Parameter Space" of Chemical Vapor Deposition Graphene Growth with Quantum Chemical Simulations,* J. Phys. Chem. C, **120**(26), 13851-13864 (2016). Received: March 15, 2016, published online: May 26, 2016, publication date: July 7, 2016. DOI: 10.1021/acs.jpcc.6b02673 Feature Article. 査読有

7. M. Jiao, W. Song, H.-J. Qian, Y. Wang, Z. Wu, **S. Irle**, Keiji Morokuma *QM/MD studies on graphene growth from small islands on the Ni(111) surface,* Nanoscale **8**(5), 3067-3074 (2016). Received: November 3, 2015, published online: January 8, 2016, publication date: February 7, 2016. DOI: 10.1039/c5nr07680c、査読有

〔学会発表〕（計　0　件）

〔図書〕（計　0　件）

〔産業財産権〕

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〔その他〕
ホームページ等

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