

Extending the length-scales of serial temperature-accelerated dynamics simulations

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Temperature-accelerated dynamics (TAD) [1] is a powerful ‘unbiased’ method to accelerate the dynamical simulations of systems with infrequent events. In this method, a basin-constrained high-temperature molecular dynamics simulation is used to determine the system evolution at low temperature. In particular, in some cases TAD can accelerate molecular dynamics simulations by factors as large as 106. As a result, for small systems TAD can be used to carry out realistic simulations of non-equilibrium processes such as thin-film growth over experimental time-scales. However, since the computational work associated with TAD scales approximately as N^3 (where N is the number of atoms in the system) this places a severe limit on the size of systems which can be simulated. One solution to this problem is the use of parallel TAD simulations [2] based on spatial decomposition combined with our synchronous sublattice (SL) algorithm [3]. Using this method, we have demonstrated [2] that TAD simulations can be carried out over extended time-scales and for very large system sizes. However, while this significantly improves the scaling, the size of activated events is limited by the decomposition size. In addition, one needs to carefully control the cycle (communication) time between processors to avoid errors in the dynamics. Accordingly, it is desirable to develop methods to improve the scaling of serial TAD. Here we discuss recent work which we have carried out in order to characterize the relevant bottlenecks and improve the scaling behavior. These include the use of a localized saddle-point method to determine the activation barrier of high-temperature events [4] as well as a local refining method [5] for identifying high-temperature transitions. By combining these methods we have found a significant improvement in the scaling of serial TAD. Possible methods for further improvement, including recent work on the development of a purely ‘local-time’ TAD, will also be discussed.

Flexible accelerated molecular dynamics with a hybrid metadynamics/hyperdynamics method

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A flexible, adaptive version of the hyperdynamics algorithm is developed by including aspects of metadynamics. A global collective variable (CV), based on an arbitrary set of local degrees of freedom, is used to represent the state of the system, thus abstracting any system-specific details from the biasing algorithm itself. A self-learning bias potential can then be generated on-the-fly through a metadynamics procedure, thus allowing the algorithm to adapt itself to the instantaneous biasing requirements of the system.

In this contribution, we will discuss this new algorithm, the collective variable-driven hyperdynamics (CVHD) method and its relation to Bond Boost hyperdynamics and infrequent metadynamics. The similarities and differences between these related methods will be highlighted, and we will show how they can complement each other. Furthermore, practical applications of the CVHD method to processes relevant to pyrolysis, conformational sampling, catalysis, and growth will be given to demonstrate the method’s strengths when applied to these very different systems, reaching boost factors of up to 10^9 compared to normal (unbiased) MD.

Does the transition state encode the rate of a driven reaction?

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In an autonomous system, reaction rates are determined by the dynamics in a small neighbourhood of the transition state. If the system is subject to external driving, it becomes difficult to define either transition states or reaction rates. Nevertheless, in some cases it is possible to identify a special trajectory of the

driven system that can serve as a transition state. Its stability properties yield macroscopic reaction rates.

Modelling static and dynamic strain ageing in FeC alloys at the atomic scale

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Modelling static and dynamic strain ageing in FeC alloys at the atomic scale

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Strain ageing of metallic alloys is a well-known phenomenon whose origin takes place at the atomic scale but with direct consequences at the macroscopic level. The yield peak and Lüders plateau are related to static strain ageing (SSA) while the Portevin-Le Chatelier (PLC) effect defined as the presence of serrations on the plastic part of stress-strain curve during tensile test is due to dynamic strain ageing (DSA). In ferritic steel these both atypical behaviors are due to the interaction between dislocations and solute atoms (mainly C). Depending on ageing time and temperature, solute atoms diffuse towards dislocations and affect their mobility. At the microscopic scale, this results most of the time in an increase of the stress required to trigger dislocation movement. At the macroscopic scale, it results in a stress peak followed by softening, this serrated behavior occurring at the elastic-plastic transition (Lüders phenomenon) and/or continuously during plastic yielding (Portevin–Le Chatelier effect). In this talk, we will present our attempt at modelling the formation of Cottrell atmospheres. To this aim, we use Molecular Dynamics, Metropolis Monte Carlo as well as the Activation Relaxation Technique (ART) and more precisely the off-lattice self-learning Kinetic-ART Monte Carlo method [El-Mellouhi2008] for both screw and edge dislocations. The kinetics of the atmosphere formation will be compared with experimental results such as those of Lavaire et al. [Lavaire2001], whereas the equilibrium Cottrell atmosphere obtained will be compared with the ones obtained previously by Metropolis Monte Carlo [Veiga2013, Veiga2015].

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The variational nature of some reaction path models

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The reaction path is a central subject in theoretical chemistry. It is a pathway imagined on the potential energy surface (PES). It provides a one-dimensional description of a chemical reaction in an N-dimensional configuration space. There are a variety of reaction path models. Each type of reaction path has advantages and inconvenients in the description of the process. We present the variational nature of the most widely used models, namely, Intrinsic Reaction Coordinate, Newton trajectory, Gradient Extremal, and Gentles Ascent Dynamic path. Extension of the Reaction Path model is also discussed.

Temperature programmed molecular dynamics

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Temperature programmed molecular dynamics (TPMD) method is a recent addition to the class of temperature accelerated schemes. TPMD can be used to efficiently study the long timescale dynamics of a material system. A situation commonly encountered in several complex materials is that the system remains trapped for long periods of time in a collection of potential basins in the energy landscape, called a superbasin. Transitions between superbasin states can be rare at molecular dynamics timescales, however, escapes from the superbasin involving larger activation barriers are even rarer. Often, it is the latter type of moves that are of interest when long timescales of seconds and beyond need to be accessed. TPMD method employs a temperature program with state-constrained molecular dynamics calculations that allows transitions of interest to happen more frequently. Separation of timescales is exploited for identifying the superbasin and selecting a superbasin escape for a move. Using TPMD method one can accurately study superbasin-to-superbasin transitions while disregarding low-barrier pathways that have been traditionally difficult to handle with rare-event simulations. I will describe some of the other key features of the TPMD method. Application of the technique to various materials problems will be discussed.

Meaningful timescales from Monte Carlo simulations of molecular systems: the case of hard disks

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A new Monte Carlo (MC) algorithm is proposed aiming at extending the timescales accessible by molecular dynamics, that combines synergistically the acceleration provided by the use of discrete potentials (as in discrete molecular dynamics) with the possibility to let the systems evolve through unphysical trajectories typical of Monte Carlo methods.

To achieve this goal, a physically meaningful timescale has to be introduced in the Monte Carlo trajectories even when simulating molecular systems evolving in a continuous space and characterized by an infinite and unknown number of states, e.g., when classical Kinetic Monte Carlo (KMC) methods cannot be applied.

As a first step in the development of the method, in this contribution a system of hard disks is considered. For such a system, the equations of motion can be written equivalently as a set of equations describing a chemical reaction network, i.e., one can identify the current state of the system with the paths traveled by the atoms. This identification allows to use a KMC scheme to solve the equations of motion, namely the stochastic simulation algorithm,[1] where the state-to-state transitions are easily determined on-the-fly and a direct link between the MC time step and the true physical time is established by using propensities proportional to the velocities.

The method was validated against discrete Molecular Dynamics. The simulation results confirm that:[2]

- 1) the position probabilities as well as the relaxation time of the global orientational order parameter and of the velocities converge to the correct results when decreasing the step size of the MC move;
- 2) the Maxwell velocity distribution is recovered directly without any need of independent samplings, as instead in traditional Metropolis MC.
- 3) the proposed algorithm provides reasonable results for the dynamics of the system at a fraction of the computational cost required by discrete Molecular Dynamics.

Additionally, since the new method maintains the same basic algorithmic structure of a conventional Kinetic Monte Carlo scheme, it can provide, in perspective, a unified numerical framework to simulate the dynamics of systems characterized by a competition between conformational relaxation and chemical reactions, as, for example, in organic light emitting diodes and enzyme catalysis.[3,4]

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Evolution of nanosize defects to experimentally relevant timescales**Gao, Fei**

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We continue to develop so called steady-state accelerated molecular dynamics (SSAMD) method to model infrequent atomic-scale events, which is applicable to the events on a rugged free-energy surface. In this method, a key new development is the time dependent evolution of a biasing hyperpotential which requires no foreknowledge of the potential energy surface. Instead, the potential is slowly increased to accelerate the dynamics, allowing the system to evolve from a steady state to another, and thus, leading to a state transition. This approach is self-evolving and can be applied to the coupled motion of fast and slow dynamics. We will demonstrate several applications of the SSAMD method, including (1) the evolution of He-V clusters, nucleation and growth of voids, as well as (2) the habit plane or Burgers vector changes of dislocation loops from $1/2\langle 111 \rangle$ to another $1/2\langle 111 \rangle$ or from $1/2\langle 111 \rangle$ to $\langle 100 \rangle$ in Fe and (3) a helium-rich He-V cluster migration by an interstitial-assisted mechanism. The SSAMD approach is also applied to study the growth of a nano He-V cluster from small clusters for times on the order of seconds. These simulations provide significant insights into defect evolution and defect interaction at experimentally relevant time-scale.

Derivation of TTT diagrams with kinetic Monte-Carlo simulations**Gupta, Ankit**

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Al-based light-weight alloys are promising for structural applications. A critical strengthening mechanism in these alloys is precipitate formation and thus the inherent evolution of the precipitates over time plays a key role in governing the mechanical behaviour of these alloys. Therefore, in order to fine tune the mechanical properties, an in-depth understanding of the precipitation kinetics is crucial. In this work, we study the precipitation kinetics in a model Al-Sc system employing kinetic Monte-Carlo (kMC) simulations. A linear bond-cutting model has been used to describe the underlying energetics. The kinetics has been analysed in terms of size distribution of the precipitates and their temporal evolution. The final results have been plotted as time-temperature-transformation (TTT) diagrams. The critical factors controlling the key features of the fully atomistically derived TTT diagrams such as asymptotic and nose temperature are discussed. Since the key observations are independent of the specific material system, they can be applied to tailor the precipitation kinetics in many applications.

Recent developments of the adaptive kinetic Monte Carlo method**Henkelman, Graeme**

(University of Texas at Austin, Institute for Computational and Engineering Science, Chemistry, Austin, USA)

Central configurations in atomic and molecular physics**Jaffé, Charles**

(West Virginia University, Chemistry, Morgantown, USA)

Central configurations are well known in celestial mechanics. The rings of Saturn and the Trojan asteroids of Jupiter are just a couple of examples. They play an important role in the dynamics of Keplerian systems. In this talk I will consider the analogous problem of the role the central configurations play in the dynamics of Coulombic systems. Through out this talk I will be using the molecular hydrogen ion, H_2^+ , and helium atom, He, as examples.

Recent improvements in NEB and minimum mode following methods

Jonsson, Hannes

(University of Iceland, Science Institute, Chemistry, Reykjavik, Iceland)

Recent improvements will be presented to methods for finding minimum energy paths and saddle points on energy surfaces so as to speed up calculations of the mechanism and rate of transitions in simulations bridging time scales. One of these is the minimum mode following method (MMF) which only requires knowledge of the initial state. In the nudged elastic band (NEB) method for finding minimum energy paths when both initial and final states are known, the calculations have typically been started using a linear interpolation between the endpoints, but an improved method based on pairwise distances, the IDPP method, will be presented. It helps avoid close encounters of atoms and speeds up the convergence. Also, a quick algorithm for aiding the assignment of atoms in the final state to atoms in the initial state has been developed for large, materials systems. For complex systems with multiple minimum energy paths, an evolutionary algorithm has been used to find a globally optimal path, i.e. one that involves smallest activation energy. An improvement in the implementation of the spring forces for distributing the images of the system along the path will also be discussed. Finally, a machine learning algorithm used to speed up the convergence to the minimum energy path will be discussed. In calculations where only the initial state is specified, the minimum mode following (MMF) method can be used to climb up the energy surface and converge on a first order saddle point. Again, the initialization of the calculation is important and a method will be presented for placing the starting points on a hypersphere with a radius that increases gradually as saddle points are harvested. The minimum mode is found by the Davidson method where a preconditioner is constructed from a BFGS approximation. With these and other improvements, the number of function evaluations needed to find all saddle points below 1.5 eV in a heptamer island benchmark has been reduced to less than a third compared with previously reported results. In addition, machine learning can be used to reduce the number of function evaluations even further.

Lessons from applications of multi-scale techniques to analysis of the permeation and selectivity in KcsA ion channel

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MD simulations are aimed to provide a mechanistic picture of the permeation of an ion through a channel. Typically, such a picture is build up via calculating the potential of mean force (free energy) by using so-called biased techniques. In such approach dynamics (fast oscillations) of the protein are averaged out whereas ion's dynamics considered as pure stochastic on more slow time scale. First we discuss the relationship between an external artificial bias and dynamics of the protein and show generic pitfalls of 'standard' biased methods. Then we consider modifications of the standard procedure and provide a picture of ion-channel interaction in KcsA channel. The emergent picture is based on a strong-correlated network of residues of the protein and ions inside the channel. Understanding interactions within the network provides the way for a consistent description of the permeation and selectivity of ions in KcsA channel.

Replica exchange Wang-Landau sampling: a new paradigm for petascale Monte Carlo simulation

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We introduce a generic, parallel Wang-Landau Monte Carlo sampling method[1] that is naturally suited for implementation on massively parallel, petaflop supercomputers. The approach introduces a replica-exchange framework involving densities of states that are determined iteratively for overlapping windows in energy space, each via traditional Wang-Landau sampling. The framework is valid for models of soft and hard condensed matter, including systems of biological interest. The significant scalability, performance advantages, and general applicability of the method are demonstrated using thousands of computing cores for several quite different models. Systems studied include those possessing discrete as well as those with continuous degrees of freedom, including those with complex free energy landscapes and topological constraints.

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Automated reaction pathway sampling using stochastic surface walking method for predicting reactions**Liu, Zhipan**

(Fudan University Shanghai, Fudan University, Dept Chemistry, Shanghai, China, People's Republic of)

In this talk, I will introduce our recent development for the SSW package, including Stochastic Surface Walking method (SSW) and Double-Ended Surface Walking (DESW) method, and apply the package for resolving the reaction pathways in catalysis and solid phase transition. The SSW method is designed for the global optimization of structure on potential energy surface (PES), while maintaining the pathway information during structure search. By adding bias potentials and performing local relaxation repeatedly, SSW method can perturb smoothly the structure from one minimum to another following a random direction. The SSW method in combination with DESW method can be utilized for finding unknown structures and predicting chemical reactivity from molecules to solids. Using these methods, we recently studied a number of important systems, e.g. ZrO₂ tetragonal-to-monoclinic phase transition, heterophase junction structures in photocatalysts, and dynamic catalyst structure evolution in H₂ evolution.

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Long-time behavior of vacancies and vacancy clusters in graphene: an accelerated quantum molecular dynamics study

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The Extended Lagrangian Born-Oppenheimer molecular dynamics formalism is used in conjunction with Parallel Replica Dynamics to obtain an accurate tool to describe the long-term dynamics of vacancy defects in graphene. Langevin dynamics have been employed at different temperatures to calculate the single vacancy diffusion coefficient in a single layered graphene sheet. The long-term behavior of a di-vacancy cluster has also been studied. This defect is extraordinarily stable and thought to be immobile. Our Parallel Replica dynamics calculations show otherwise. We run for more than $1 \mu\text{s}$ and we observe the net translation of the center of mass of the complex defect. We have analyzed the pathway and the energy barriers for this translation and compare the results with available experimental data with satisfactory agreement.

The kinetic activation-relaxation technique: an off-lattice kinetic Monte Carlo method with on-the-fly topological cataloguing

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In spite of considerable advances in computational capacities over the last decades, there remains a considerable gap between experimentally relevant time scales and those accessible to atomistic simulations. This gap reflects the fundamentally multi scale nature of atomistic kinetics that can only be lifted partially through approximate methods that attempt to capture the most important aspect of specific phenomena. Among those approaches, the kinetic activation-relaxation technique (k-ART) is an off-lattice kinetic Monte Carlo with on-the-fly cataloguing capabilities that allows fully atomistic second-long and more simulations of complex and large scale alloys and disordered systems such as amorphous silicon and steels, while incorporating exactly elastic effects. In this talk, I'll present the k-ART method, recent applications to various systems and its advantages and limitations in the study of complex materials.

Bridging space-time scales in the field of diffusion-controlled phase transformations

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Bridging space-time scales in the field of diffusion-controlled phase transformations is generally based on the concept of local equilibrium. The most notable example of this is the thermodynamics of irreversible processes. However, within the Self Consistent Mean Field (SCMF) theory, it is shown that diffusion in alloys, spinodal decomposition and more generally kinetics of nanoscale composition fluctuations are correctly described only if deviations of short range order from local equilibrium are accounted for. Local equilibrium assumptions are still useful when applied at intermediate space-time scales. For example, in dilute solid solutions including isolated point-defect solute clusters, by means of a local equilibrium hypothesis within every cluster, it is possible to introduce a rigorous definition of non-equilibrium transport coefficients and decompose them into mobilities and association-dissociation rates of clusters. It is then explained how the restricted use of the local equilibrium concept extends the scope of mesoscopic kinetic simulation methods such as cluster dynamics and phase field methods. Applications in the field of phase stability under irradiation are presented. Starting from an ab initio calculation of vacancy, split interstitial and interstitial migration barriers, dynamic phase diagrams and radiation-induced segregation at grain-boundaries are predicted in Fe-based dilute alloys including metallic solutes, C, O and N interstitial impurities and concentrated Fe-Cr alloys. Some of these predictions are then compared to

direct atomistic kinetic Monte Carlo simulations and experimental observations.

Ab initio artificial neural network kinetic Monte Carlo simulations in iron alloys

Olsson, Pär

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Longtime atomistic simulations with parallel trajectory splicing

Perez, Danny

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Molecular Dynamics (MD) is a workhorse of computational materials science. Indeed, MD can in principle be used to obtain any thermodynamic or kinetic quantity, without introducing approximation or assumptions beyond the adequacy of the interaction potential. This enviable quality however comes at a steep computational price, hence limiting the system sizes and simulation times that can be achieved in practice. While the size limitation can be efficiently addressed with massively parallel implementations of MD based on spatial decomposition strategies, the same approach usually cannot extend the timescales much beyond microseconds. In this talk, we discuss a novel approach --- Parallel Trajectory Splicing (ParSplice) --- that aims at addressing the timescale limitation of MD for systems that evolve through rare state-to-state transitions. As with the Parallel Replica Dynamics method, the problem is instead parallelized in the time domain. The key innovation of ParSplice lies in the use of speculation on the future evolution of the dynamical trajectory. This exposes additional parallelism by allowing work to simultaneously proceed in many states. Predictions are carried out through a concurrent stochastic simulation parameterized on the fly. We review the formal underpinnings of the method and demonstrate that it can provide arbitrarily accurate results while providing significant improvement in computational efficiency compared to its predecessors. We then illustrate the usefulness of ParSplice by presenting different examples of materials simulations where access to long timescales was essential to access the physical regime of interest.

Carbon diffusion in supersaturated ferrite

Perez, Michel

(Université de Lyon, MATEIS - INSA, Villeurbanne Cedex,)

Hillert's mean-field elastic prediction of the diffusivity of carbon in ferrite is regularly used to explain the experimental observation of slow diffusion of carbon in supersaturated ferrite. With increasing carbon supersaturation, the appropriateness of assuming that many-body carbon interactions can be ignored needs to be re-examined. In this work, we have sought to evaluate the limits of such mean-field predictions for activation barrier prediction by comparing such models with molecular dynamics simulations. The results of this analysis show that even at extremely high levels of supersaturation (up to 8 at% C), mean-field elasticity models can be used with confidence when the effects of carbon concentration on the energy of carbon at octahedral and tetrahedral sites are considered. The reasons for this finding and its consequences are discussed.

Newton trajectories in mechanochemistry

Quapp, Wolfgang

(Universität Leipzig, Mathematisches Institut, Fakultät für Mathematik und Informatik, Leipzig, Germany)

Considerable interest is attached to the problem of mechanical stress to a chemical reaction. We use the concepts of reaction path (RP) by Newton

trajectories (NT) on a potential energy surface (PES).

The RP is a central subject in theoretical chemistry. It provides a one-dimensional description of a chemical reaction in an N-dimensional configuration space.

Additionally, one can apply mechanical stress in a defined direction to the molecule and generate an effective PES. Changes for minimums and saddles by the stress are described by Newton trajectories on the original PES [1].

The barrier of a reaction fully breaks down for a maximal rupture force of the norm of the gradient of the PES along a pulling Newton trajectory.

This point is named barrier breakdown point (BBP).

We discuss topologically different, 2-dimensional examples for this model

to understand and classify some aspects of the mechanochemistry of molecules.

Further properties of mechanochemistry are explained with the help of NTs.

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Transition state theory for solvated reactions beyond recrossing-free dividing surfaces

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The accuracy of rate constants calculated using transition state theory depends crucially on the correct identification of a recrossing-free dividing surface.

We show here that it is possible to define such optimal dividing surface in systems with non-Markovian friction. However, a more direct approach to rate calculation is based on invariant manifolds and avoids the use of a dividing surface altogether. Using that method we obtain an explicit expression for the rate of crossing an anharmonic potential barrier. The excellent performance of our method is illustrated with an application to a realistic model for LiNC \rightarrow LiCN isomerization.

Normal form approach to transition state theory

Schubert, Roman

(University of Bristol, Mathematics, Bristol, United Kingdom)

Applications of stochastic surface walking method in molecular crystal structure prediction

Shang, Cheng

(Fudan University, Shanghai, China, People's Republic of)

An important scientific problem for many chemical industries, who produce organic semi-conductor, dye, porous molecular materials and drugs, is how to obtain the structure of molecular crystal and understand their chemical properties. With the development of simulation methods, it is possible to theoretically predict structures of simple molecular crystals. However, for complex pharmaceutical molecules, we still need an efficient method to explore the potential energy surface of any given molecule, predicting their crystal structures and search the minimum energy pathway for possible phase transition. Recently, we have developed a new method for molecular crystal structure prediction and mechanism investigation of possible phase transition. The new method bases on the stochastic surface walking method (SSW), combining with the first principle calculation and empirical force field calculation. Using this method, we have investigated some simple molecules, characterized the potential energy surface of any molecular

crystals in general.

Identifying and enhancing important fluctuations for sampling molecular systems with rare events

Tiwary, Pratyush

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In modern-day simulations of many-body systems, much of the computational complexity is shifted to an almost prescient identification of low-dimensional slowly changing molecular order parameters or collective variables (CVs). A vast array of enhanced-sampling methods are based on the identification and biasing of these CVs, whose fluctuations are important in driving the rare events of interest. Here, I will describe a new algorithm [1] called spectral gap optimization of order parameters (SGOOP) for finding such optimal low-dimensional CVs for sampling molecular systems with rare events, given a much larger set of candidate CVs. SGOOP is based on the idea that the best CV displays the maximum separation of timescales, or spectral gap, between visible slow and hidden fast processes. The spectral gap is calculated through a maximum path entropy or Caliber based model that uses limited prior static and dynamic information about the system. Finally, I will show some applications of SGOOP and related methods [3] with a special focus on kinetics of drug unbinding with classical MD.

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Using enhanced sampling to study the formation of crystals

Tribello, Gareth

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There are now a wide variety of different enhanced sampling methods that can be used to ensure that rare events occur during the relatively-short timescales that are accessible in molecular dynamics simulations and to extract free energy surface. The key question for the community is thus: what new insight can be extracted using these methodologies. In my talk I will discuss the work that I and others have done using these techniques to study the formation of crystals. I will explain what I think has been achieved and the problems that still remain to be solved.

Topological clustering in free energy methods

Triguero de Prades, Carlos

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The capability to identify and time-track molecular clusters is an important resource to study a variety of processes in different research fields based on atomistic simulations. The process whereby the clusters are defined is based on some connectivity criteria between the set of elements subject to the clustering.

The detection of clusters in condensed phases is rather simple, and can be performed independently of the environment (solvent) in which the elements are embedded. Subsequently, the environment phase neither matters. A distance threshold between the elements can be used as a connectivity criteria. For solid phases we can even exploit the phase symmetries for example, to detect crystalline domains. The distance-based clustering works while it is possible to define a characteristic length scale from the first-neighbour distance distribution of the elements to cluster.

The recognition of \$non-condensed\$ \$clusters\$ embedded in condensed phases is more complex. The first-neighbour distance distribution between the elements to cluster is wider and larger compared to that obtained for the environment. Hence, the definition of a \$characteristic\$ \$distance\$ is not realistic, and the clustering based on the distance fails. This is the typical scenario for gas-bubble nucleation in a liquid. In this case the effect of the environment is \$crucial\$. A \$new\$ \$connectivity\$ \$criteria\$ taking into account the role of the environment as a \$cluster\$ \$container\$ needs to be defined.

We present a new \$topological-connectivity\$ \$criteria\$ from which the detection of \$connected\$ \$domains\$ is \$robust\$ (not metric based, recognizes the clusters as entities). It extends the detection of molecular clusters in condensed environments when they are not condensed. Different collective variables can be defined from the \$continuous\$ \$adjacency\$ \$matrix\$ associated to this new \$topological-clustering\$. They can be used in the available \$free\$ \$energy\$ \$methods\$ to access the \$free\$ \$energy\$ \$manifold\$, for example the free energy as a function of the cluster size. Similar collective variables can be defined for the distance-based clustering, and we show how the system rapidly finds paths to make these variables not representative.

Parallel trajectory splicing simulations of cation dynamics in pyrochlore

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Parallel Trajectory Splicing Simulations of Cation Dynamics in Pyrochlore

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In many systems, dynamics are often characterized by more than one time scale. In the case of complex oxides such as pyrochlore ($A_2B_2O_7$), cation dynamics are typically much slower than anion dynamics. The dynamics in this system is further complicated by cation disorder, in which the A and B cations are mixed, which leads to a situation in which each local cation environment is unique. Thus, simulating cation transport in pyrochlore involves a complicated potential energy landscape. Accelerated molecular dynamics methods are one powerful approach to study such systems. In particular, parallel replica dynamics (ParRep) and parallel trajectory splicing (ParSplice), a recent advance of ParRep, provide an important feature in which transitions from one state to another only need to be detected, not characterized. In this work, we study cation dynamics in pyrochlore using ParSplice, defining transitions to be movement of cations. We consider the evolution of both cation interstitials and cation vacancies in pyrochlore as a function of cation disorder. We find that the dynamics of both defects is complex, characterized by the restoration of cation order as the defect migrates through the material. Further, the rate of migration depends on the level of disorder and thus changes as the material reorders. We speculate the existence of an antisite percolation network above a disorder threshold, which allows for the fast diffusion of cations. This is in marked contrast with results on oxygen diffusion, which showed a monotonic increase of the ionic diffusivity with increasing disorder in the same compound. These results highlight the dynamic interplay between cation diffusion and the recovery of disorder and has important implications for understanding radiation damage evolution, sintering and aging of these materials.?

Speculatively parallelized temperature accelerated dynamics

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Speculatively parallelized temperature accelerated dynamics

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Temperature accelerated dynamics (TAD) is a powerful atomistic approach for reaching long time scales for systems whose dynamics are characterized by activated processes, especially when the energy barriers are high. In TAD, a basin-confined simulation at a high temperature is employed to discover attempted escape events in a way that allows the assignment of a time t_{low} (approximate, but controllably accurate) for the same event occurring in a hypothetical trajectory at the lower, proper temperature. High- and low-temperature escape times typically will not occur in the same order, as high-barrier processes are sped up more by the increase in temperature. After the basin-confined, high-temperature trajectory has reached a certain total time (t_{stop}), one can say with a specified confidence that the first escape event at low temperature has been observed. The system is then moved to the new state corresponding to this event, the clock is advanced by t_{low} for this event, and the TAD procedure is begun again in the new state.

In this talk, I will describe a novel approach for parallelizing TAD: speculatively parallelized TAD (SpecTAD) [1]. In SpecTAD, we spawn a child process in parallel each time an attempted escape event is observed, if it has a chance of becoming the accepted event. This child process, which corresponds to a complete, independent TAD simulation in the state to which the system made its attempted escape, is continued until and unless it becomes clear that this event is not the one that will be accepted by the parent TAD simulation. SpecTAD gives a significant additional speedup over conventional TAD when t_{stop} is much longer than the time at which the ultimately accepted event is first attempted. A SpecTAD trajectory can advance from state to state as rapidly as the (correct) transitions occur at high temperature. Moreover, this approach can be combined efficiently with the use of parallel replica dynamics to accumulate the high-temperature time more quickly. I will describe the SpecTAD method, give examples of its application, and discuss situations where its ability to eliminate the waiting time until t_{stop} introduces new possibilities for simulations that would be unfeasible with conventional TAD.

[1] R.J. Zamora, B.P. Uberuaga, D. Perez, and A.F. Voter, The modern temperature-accelerated dynamics approach. *The Annual Review of Chemical and Biomolecular Engineering* 7, 3.1-3.24, (2016).

The geometry of reactions of rotating molecules

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Recently, the phase space structures governing reaction dynamics in Hamiltonian systems have been identified and algorithms for their explicit construction have been developed. These phase space structures consist of invariant manifolds whose existence is induced by saddle type equilibrium points which are characteristic for reaction type dynamics. The main algorithms to construct the phase space structures are based on a Poincare–Birkhoff normal form. Using tools from the geometric theory of Hamiltonian systems and their reduction, we show in this talk how this construction of these phase space structures can be generalized to the case of the relative equilibria of a rotational symmetry reduced N-body system. As rotations almost always play an important role in the reaction dynamics of molecules, the approach presented in this talk is of great relevance for applications.

Formation of carbon Cottrell atmospheres and their effect on the stress field around an edge dislocation

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Biased Metropolis Monte-Carlo is employed to build carbon Cottrell atmosphere around an edge dislocation. A novel method involving only local minimisation during the Metropolis scheme allows to deal with million atom system within a reasonable computation time. It is found that (i) the carbon atoms occupy interstitial sites not only in the traction zone, but also in the compression zone; (ii) local carbon concentrations of approximately 10% are in good agreements with experimental values; (iii) the saturation of the Cottrell atmosphere does not originate from the stress-field around the atmosphere but from repulsive carbon-carbon interactions only.

Defect evolution in structural materials from SEAKMC simulations: opportunities and challenges

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Radiation induced defects in structural materials for nuclear energy systems control the microstructural evolution and changes in material properties. In this study, defect evolution beyond the time scale of conventional molecular dynamics has been investigated using self-evolving atomistic kinetic Monte Carlo (SEAKMC) method. Particular examples include the formation mechanism of $\langle 100 \rangle$ loops in bcc iron and Fe-Cr alloy systems, the transformation of C15 interstitial clusters with Laves structure, and point defect interaction with a dislocation. These studies provide fundamental insights into defect interaction and evolution that may provide a basis to increase the radiation resistance of these materials. In addition, the opportunities and challenges of applying the on-the-fly KMC up to experimental time scale will be discussed; the unique predictive capabilities and the limitations of SEAKMC as well as its potential applications to a wide range of problems will be outlined.

Pathway and free energy barriers of rupturing the hemi-fission intermediate under tension: a Wang-Landau sampling study

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Membrane fission and fusion play essential roles in vesicular trafficking, such as endocytosis. Fission is a process of division of an initially continuous membrane into two separated ones, which is mediated by proteins (e.g. dynamin-family members). By contrast to fusion, however, molecular mechanisms of dynamin-mediated fission remain poorly understood. In this work, we try to obtain a better understanding of it through exploring its feasible transition pathways and corresponding free energy landscapes in computer simulations.

It has been verified from recent experiments and simulation studies that membrane fission could be completed through a *stable* hemi-fission intermediate, a state of two-capped membrane tubes bridged by a cylindrical micelle. To evaluate the stability of the hemi-fission intermediate, we employ advanced sampling techniques (Wang-Landau sampling in our case) to investigate the free energy barriers of rupturing the hemi-fission state. Within the solvent-free model of lipid membrane, we fix the chemical potential of the lipids, i.e., the total number of lipids in the simulation box can vary along the transformation path. It turns out that two reaction coordinates are required to completely characterize the path of rupturing the hemi-fission intermediate: (i) the total number of lipids, N , and (ii) the inhomogeneity, α , of particles distributed along the cylinder axis, which characterizes the extent of localized constriction. Through free energy calculations, we identify the transition states as those hourglass-shaped micelle-cylinder membrane, and conclude that the free energy barriers can be decreased by imposing a tension.