Scientific Report for EPSD Short Visit Grant 4369

Applicant: **Dr. S. Hallerberg**
Host: **Dr. A. S. de Wijn**
Title: **Statistical inference of precursors for long jumps in molecular diffusion (return visit)**

1 Details of the Visit

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- **To:** Dr. A. S. de Wijn
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2 Background

The diffusion of molecules on substrates is an important issue for the construction and control of nano-scale structures. Long jumps in the surface diffusion of molecules and molecular aggregates have been experimentally observed [1] and were also found in numerical simulations [2]. Recent studies [3, 4] highlight the existence of a relation between the diffusion of the molecules and the dynamics of their internal degrees of freedom. With frozen internal degrees of freedom and no thermal noise, molecular dynamics simulations of benzene on graphite show ballistic motion or super-diffusion, governed by long ballistic jumps. However, the full system, with dynamical internal degrees of freedom, exhibits normal diffusion with intermittent super-diffusive long jumps, leading to a relatively large diffusion constant. Benzene on graphite is a prototype system in which these long jumps can be further investigated.

3 Purpose of collaboration

The goal of the collaboration between host and applicant is to determine the physical mechanism which triggers the long jumps by statistical inference of specific behavior that precedes long jumps in molecular dynamics simulations, also known as a *precursor* or *predictor*. Precursors are typically discussed for short range predictions of events, such as earthquakes, epileptic seizures, or turbulent wind gusts [5]. They are especially useful to characterize rare events, such as the long jumps under consideration, since rare events are not well represented in quantities that are based on averaging over the whole data set, such as cross-correlation functions. In the context of this project, the focus is not on the forecast, but on the precursor itself, and the information it provides about the mechanism of long jumps.

During three previous visits (one of them was founded by the ESF) we have determined a number of likely candidate mechanism that lead to long jumps. We applied the classification algorithm in order to uncover a relation between the temporal changes in the energy distribution among the molecule's internal degrees of freedom and the long jumps. More precisely, we found that low energies in the torsion modes of the molecule coincide with long super-diffusive jumps.

4 Work carried out during the visit

Since our last visit, Dr. de Wijn has run a number of simulations with damping of the torsion modes. This damping reduces the energy in the torsional degrees of freedom, thus creating the precursors. We expected that this would lead to more long jumps, enhancing diffusion. However, though the long jumps tend to be longer, they occur less frequently. We therefore assumed that there is a second physical mechanism involved the diffusive behavior that is also triggered by the precursors in the torsion modes, namely "long sticks". As a stick we consider a long jump with zero velocity, during which the molecule remains in a small vicinity for a long time without diffusing. In order to test this, we have designed an additional filter for long sticks.

During the proposed visit we tested and improved this long stick filter and we repeated the statistical analysis of the data sets that we have previously performed for long jumps in order to identify precursors of long sticks. In more detail, we estimated distributions of duration and return-time distributions of long sticks and we tested via a classification approach, whether typical signatures in the energy distribution coincide with long sticks.

Furthermore, we applied the newly developed and the existing programs and scripts to the new data sets that resulted from the simulations with damped torsion.

An important result of this visit is that fluctuations in the energy of certain modes coincide not only with super-diffusive jumps but also with sub-diffusive sticks. This allows us to explain, why damping specific modes affected the diffusion coefficient in a way that was contradictory to our previous understanding of the problem focusing only on long jumps. Another result of this visit is that the relevant modes for triggering anomalous movements (both jumps and sticks) are not only the torsion modes of the molecule. Remarkably, we found that the modes that provide useful precursors for long-sticks are exaclty the ones that lead to changes in the diffusion coefficient, when damped. In other words, changes of the energy in certain modes and their relation to single jumps and sticks provide a microscopic description of the effect we observed in a macroscopic quantity, i.e., the diffusion coefficient. All these results will be discussed in more detail in a publication, that we started to write during the visit.

5 Future collaborations

An additional goal of the visit was to discuss our specific issue of the diffusion of benzene on graphite in the general context of anomalous diffusion in dynamical systems (see for instance [6, 7]). A theoretical explanation of anomalous diffusion of electrons in periodic potential [6] has been done by understanding the system as a chaotic Hamiltonian system [7]. The diffusive motion of a single particle such as an electron or an adatom has been shown to be determined by its stickiness in the vicinity of stable tori. Anomalous diffusion has been so far studied for electrons [6] or other particles without internal degrees of freedom [8] moving in periodic potentials. However, in our example we consider a molecule with internal degrees of freedom as a diffusing particle. Previous studies showed that he effects of the internal degrees of freedom of the molecule on the motion of its center of mass cannot be neglected [3, 4]. On the other hand, including the internal degrees of freedom generates a Hamiltonian System with a 36-dimensional phase space. Hence, we have to deal with the question whether it is possible to transfer existing concepts for anomalous transport in two-dimensional Hamiltonian systems, to systems with a high-dimensional phase space. Since it was not possible to answer this complex question sufficiently within one week of visit, we developed an idea for a future collaboration that aims on answering it (for the special case of the system, we are studying).

6 References

References

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