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Simulating charge transport in flexible systems ☆

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Summary Systems in which movements occur on two significantly different time domains, such as organic electronic components with flexible molecules, require different simulation techniques for the two time scales. In the case of molecular electronics, charge transport is complicated by the several different mechanisms (and theoretical models) that apply in different cases. We cannot yet combine time scales of molecular and electronic movement in simulations of real systems. This review describes our progress towards this goal.

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Introduction

Simulating conventional silicon-based electronic devices is a task centred on describing the movement of charge carriers (holes or electrons) using well-established quantum mechanical techniques (Ortmann and Roche, 2013). However, many of the formalisms involved (e.g., Marcus theory (Marcus, 1964) or Landauer Theory (Emberly and Kirczenow, 2000)) assume a specific mechanism for charge transport and are unable to treat systems in which several different mechanisms are possible. This does not represent a problem for conventional crystalline semiconductors, where the charge-transport mechanisms are well defined, but leads to serious ambiguities for organic or biological systems. For instance, the now well-established hopping mechanism for charge-transport in DNA was long quite controversial (Jortner et al., 1998; Giese, 2000).

Simulating less conventional electronic devices whose active components consist of flexible organic molecules or simulating charge-transfer in proteins and other biological systems introduces a further degree of complexity. In these cases, the molecular scaffold that serves as the basis for the electronic transport properties of the system is itself dynamic. Furthermore, the time scale of the conformational movements of the molecular scaffold (tens of picoseconds or longer) (Ishikawa et al., 2008) is far longer than that of electro- or hole migration (femtoseconds or faster) (Remacle and Levine, 2006). Thus, we are faced with a classical multiscale problem of linking disparate time scales. The less-than-ideal expression ''multiphysics'' has been used to describe such problems, in which different physical models (but not different physics) are combined within one simulation (Keyes et al., 2013). Often, the situation is complicated further in organic and biological systems because the binding nature of the constituent molecules changes are charges added or removed (Shubina et al., 2014), so that classical force fields are not appropriate.

This all amounts to a formidable simulation problem that can currently only be solved by performing extremely computationally expensive direct quantum mechanical molecular dynamics (MD) simulations. These are not feasible for the large systems of interest in organic electronics and will not be for several decades. This chapter describes some attempts to address some of the problems and progress towards a complete solution. This solution is still far away, so that what follows has the character of a progress report (Clark et al., 2013).

Classical molecular dynamics

The accepted technique for simulating organic and biological conformational dynamics is molecular dynamics (Sutmann, 2002) based on classical force fields (Monticelli and Tieleman, 2013). Such techniques, which are mathematically and computationally relative simple, can be used routinely for systems of a million atoms or more, making representative models of organic electronic devices accessible. The necessary force fields must often be developed explicitly for the application, especially for the organic semiconductor moieties and for inorganic/organic interfaces. It is most convenient to use 2D-periodic boundary conditions, rather than the 3D-variation usually used for biological simulations. This limits the programmes that can be used. In order to make association and dissociation of organic molecules (usually components of self-assembled monolayers, SAMs) on inorganic substrates possible, no formal bonds are defined between the two. The interaction between organic absorbate and inorganic substrate is best described purely electrostatically. This represents a significant difference to most SAM-simulations, which were used to investigate thiolate ligands absorbed on gold surfaces and therefore use classical covalent Au—S bond potentials. However, the relative speed and good scaling properties of classical MD simulations make them ideal for studying the morphology of SAMs and SAM-based devices (Novak et al., 2010). This can even be true for large-scale domain structures, which can form in simulations of 1 μs or less. This is illustrated in Fig. 1, which shows a snapshot from a simulation of a SAM formed by 1-benzothieno[3,2-b]benzothiophene (BTBT)-substituted alkyl phosphonate, **1**.

Fig. 2 has been colour-coded to make the different domains clear. The largest (red) domain exhibits the so-called herringbone crystalline structure and extends over approximately half of the simulated area. Smaller alternative herringbone domains (purple), ones in which the BTBT-groups form more or less parallel stacks (blue) and those in which no ordered structures are obvious (green) can also be seen. This picture, which is consistent with X-ray measurements, provides unique detail of the molecular structure of the SAM. The simulations have also proven to be able to reproduce quite subtle effects caused by changes in the structure of the SAM-forming molecules, even changing the alkyl chain-length by one CH_2-group.

Simple multi-scale models

Such classical simulations are well-established tools in both life- and nano-science but they do not provide information about the electronic characteristics of the systems. Strictly speaking, it would be necessary to simulate both the nuclear (atomic) movements and the wavefunction of the entire system simultaneously using so-called direct MD simulations (i.e., ones in which the energy and the forces are calculated quantum mechanically, rather than with a force field). This is, however, very expensive ion terms of computer time and limited in the size of the systems that can be treated. We therefore resort to a simple type of multi-scale simulation,