A Keldysh-Langevin approach to modelling nuclear dynamics in molecular junctions

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The quintessential system which is used to observe and study the effects of quantum transport is that of the molecular junction: a molecular bridge bonded between two macroscopic conducting leads. Molecules in molecular junctions are subject to current-induced forces that can break chemical bonds, induce reactions, destabilize molecular geometry, and halt the operation of the junction. Additionally, novel phenomena such as telegraphic switching and localised heating have the possibility of being exploited for device functionality. We develop a nonequilibrium Green's function based transport theory in which atoms on the molecular bridge are allowed to move. This is achieved by utilising the inherent separation of timescales between slow nuclear motion and fast electronic dynamics, allowing us to solve for the adiabatic Green's functions along with non-adiabatic dynamical corrections. To make the theoretical approach fully self-consistent, the same time-separation approach is used to develop expressions for the adiabatic, dissipative, and stochastic components of current-induced forces in terms of adiabatic Green's functions. Using these current induced forces, the equation of motion for the nuclear degrees of freedom is cast in the form of a Langevin equation. This model is applied for both static and AC driving in the leads [1] and incorporates the motion of the atoms in the central region along with the atoms on the leads interface [2]. Furthermore, we utilise a Fokker-Planck description for the classical coordinate in order to calculate Kramers' first-passage times and reaction rates [3]. We observe localized heating effects and the formation of bi-stable effective potentials for the classical coordinates which are analysed through the use of the measured noise in the current [2,3]. Negative viscosities are shown to emerge under an applied voltage bias in a variety of systems, which demonstrates the lack of a possible steady-state for certain configurations [2,4]. An applied AC driving is shown to be capable of producing a cooling effect to the molecular bridge, increasing the stability and longevity of the system [1]. We assess the validity of the Langevin approach in different regimes by applying a novel time-stepping algorithm to solve for the classical Ehrenfest dynamics of the molecular bridge and find that the results produced by the Langevin method are accurate provided that the applicable regimes are not abused [4].

[1] R. Preston, T. Honeychurch, and D. Kosov, J. Chem. Phys. 153, (2020).

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[3] R. Preston, M. Gelin, and D. Kosov, J. Chem. Phys. 154, (2021).

[4] R. Preston, T. Honeychurch, and D. Kosov, arXiv:2204.08278, (2022).