Free energies for rare events: Temperature accelerated MD & MC

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Abstract:
The talk addresses the important challenge associated for MD/MC practitioners to rare events, events whose statistical properties cannot be computed by brute force simulations. In particular we present a recent technique, useful to compute the free energy landscape associated with activated processes, and we illustrate it in a simple but instructive case. The technique derives from a procedure, introduced by E. Vanden Eijnden & L. Maragliano (Chem. Phys. Lett. 426, 168 (2006); Single-sweep methods for free energy calculations, J. Chem. Phys., 2008, 128, 184110), called TAMD, which gets the free energy landscape, in few collective variables (CV's) by extending the phase space of the system with few collective variables taken as new, slow, degrees of freedom, coupled to the original system by a suitable biasing potential. The extended system can be let to evolve for the fast, physical, variables at the physical temperature while the slow variables are thermostatted at a much higher temperature. The result is that the system can be shown to evolve sampling the full free energy landscape in spite of the presence of rare events. When, as frequent in applications, the CV's cannot be expresses in a analytical form, the procedure can be improved by a temperature accelerated Monte Carlo (TAMC) since, then, the MC "evolution" needs only the energies and no more the forces associated to the sampling. The new techniques will be demonstrated and, then, illustrated with the characterization of a simple nucleation process.

Ionic charge transport in an external magnetic field via molecular dynamics
(aka the Quest for the ionic Hall effect)

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Molecular dynamics simulations of ionic charge transport in condensed phase systems subject to an external magnetic field are relatively uncommon. This is due to two main difficulties. First, the non-canonical form of the Hamiltonian breaks time reversal invariance and key statistical relations do not hold in standard form. Second, the coupling between coordinates and momenta induced by the Lorentz force hinders straightforward application of common algorithms (e.g. velocity Verlet) and of the periodic boundary conditions usually applied for bulk simulations.

In this talk, I shall present some recent work addressing these difficulties. A generalized time reversal operation will be described and used to derive a symmetry relation for time correlation functions that do not require changing the sign of the field upon time reversal [1]. This is to be contrasted with the Kubo result [2] in which the sign of the magnetic field does change, thus establishing a symmetry relation between two *distinct* physical systems. A new, symplectic, algorithm to integrate the equation of motions will also be presented together with an adapted thermalization mechanism, which extends Nose-Hoover thermostatting to these systems [3].

These formal and practical tools will be used to discuss charge transport properties in molten NaCl and in the superionic phase of AgI, with specific focus on detecting the possible on-set of the ionic Hall effect in these systems.

[1] S. Bonella, G. Ciccotti and L. Rondoni EPL 108 60004 (2014)
[2] R. Kubo J. Phys. Soc. Jpn. 12 570 (1957)
[3] F. Mouhat, S. Bonella and C. Pierleoni Mol. Phys. 111 3651 (2013)