

Effective simulation methods for highly charged polymers

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Computer simulations have been a very useful tool in furthering our understanding of the properties of polymers. For polymers with charges along the backbone, so-called polyelectrolytes, the computational effort becomes more complex due to the long-ranged character of the Coulomb interaction. Since the interaction decreases inversely with separation no sensible truncation of the interaction potential can be applied. All pair-wise interactions have to be calculated and this provides a limit on the number of charged particles that can be considered in a simulation. The long-ranged interaction also prohibits the use of standard parallel computational techniques such as domain decomposition.

In the strong interaction regime, polyelectrolyte configurations may, in practice, become trapped indefinitely in deep local minima of the sample space and thus renders the sampling process ineffective in exploring phase space. In this talk we discuss in detail the performance of three different approaches that have been used to speed up Monte Carlo (MC) simulations of polyelectrolytes:

Clothed global moves When counterions are moved with the polyelectrolyte backbone and are not left behind when a substantial part of the chain is moved, the resulting energy changes are smaller which in turn increase the acceptance rate. For moderately charged systems the speed-up has earlier been shown to be 120 to 300 %. We show how, for systems with strong electrostatic interactions, much larger efficiency gains in the simulation process can be obtained (> 10000 %).

Parallel expanded ensembles A number of conventional MC simulations are carried out in parallel, with only one parameter being different. If this parameter is the temperature the method is referred to as parallel tempering. By allowing the different simulations to communicate and exchange conformations, those configurations that have been trapped in low temperature runs may escape via the higher temperatures runs. Thus the creation of an extra simulation dimension provides a route to circumvent high barriers in the free energy landscape, without having to climb over them directly. We show how this method scales linearly up to 8 processors for highly charged polyelectrolytes.

Parallel flat histogram simulations We describe a method of parallelising flat histogram Monte Carlo simulations, which give the free energy of a molecular system as an output. In the serial version, a constant probability distribution, as a function of any system parameter, is calculated by updating an external potential which is added to the system Hamiltonian. This external potential is related to the free energy. In the parallel implementation, the simulation is distributed on to different processors. With regular intervals the modifying potential is summed over all processors and distributed back to every processor, thus spreading the information of which parts of parameter space have been explored. This implementation is shown to decrease the execution time linearly with added number of processors.