Path Integral Grand Canonical Adaptive Resolution Simulations (PI-GC-AdResS)

Extension of Adaptive Resolution Path Integral Molecular Dynamics techniques to the study of hydrophobic molecules in and out of equilibrium

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In Short

- We will improve our current PI-GC-AdResS methods by implementing ring-contraction PI techniques and more accurate PI water models within our recently-developed AdResS framework which boasts increased computational efficiency.
- Non-equilibrium molecular dynamics (NEMD) will be introduced in this framework through the addition of a tunable electric field within simulations.
- Changes in the solvation shell structure surrounding a hydrophobic alanine dipeptide will be explored via NEMD as a function of frequency and amplitude of the electric field.
- Data from these simulations will yield important insights into the nature of water solvation of hydrophobic particles.

Background and Motivation

The solvation and aggregation of hydrophobic molecules are the subjects of intense research in the fields of chemistry, physics, and biology [1]. Fullerene, for example, is one such molecule under this microscope due to its aggregation in water and the environmental implications of this process. For this reason, a microscopic model of solvation and aggregation of fullerene is highly-sought after [2]. The physio-chemical properties of aqueous solvation are particularly well-suited for study via molecular dynamics (MD). However, today's MD simulations of condensed matter systems are increasingly characterized by demands for higher accuracy, larger systems, and longer time scales—all at the expense of enormous computational resources. Our group attempts to circumvent this issue by developing and utilizing the grand canonical adaptive resolution simulation (GC-AdResS) approach [3]. This aims to eliminate the need for prohibitively large resources by representing only the region of specific interest in high resolution while the "bulk" of the simulation is represented by a low resolution description. This method allows for a significant speedup in calculation without sacrificing the accuracy and validity of results pulled from the high-resolution region of interest. In the context of the solvation process, it is interesting to consider thermodynamic properties at the highest resolution possible, i.e., the quantum level, because quantum effects, namely delocalization of light atoms in space, is thought to have an impact on the structure of water, even at room temperature.

A popular method for incorporating these delocalization effects in simulation, ring polymer path integral molecular dynamics (PIMD) [5], increases computational load dramatically with respect to ordinary MD, inhibiting the sufficient study of large systems (for example, large solutes in aqueous baths). To combat this, the PIMD approach was integrated into the GC-AdResS framework, yielding path integral grand canonical adaptive resolution simulation (PI-GC-AdResS) which has aided in the study, at a quantum level, of static and dynamic properties of liquid water, large hydrophobic solutes, and more which would otherwise be impossible without massive computational effort [6].

Despite the success of these studies, there is room for improvement. Since the conception of PI-GC-AdResS, our group has enhanced the standard GC-AdResS, boosting its efficiency by almost 2.5x, while also making strides towards coupling high-resolution regions with continuum regions [7]. Additionally, efficient PIMD methods such as ring polymer contraction [8] are not currently supported and newer, more accurate water models have not been tested [9] (previous studies utilized one of the most simple PI water models, q-SPC/FW).

On top of the possible technical refinements outlined above, PI-GC-AdResS as a tool to better understand the structure and thermodynamics of aqueous solvation would benefit greatly from its extension to the study of non-equilibrium situations. Here, the system is perturbed by an external agent and the effects of this perturbation are observed and quantified. In the case of the solvation of a solute such as fullerene, the perturbation on the system could take the form of a localized electric field acting on the water molecules of the solvation region. The relevancy of an electric field acting as the perturbing agent stems from the idea that its modulation of the solvation shell surrounding a hydrophobic molecule will likely encourage or discourage interaction with

similarly-solvated molecules within close proximity. Thus, introducing non-equilibrium capabilities to PI-GC-AdResS will allow our group to gather novel information about aggregation of hydrophobic molecules valuable to many researchers across multiple disciplines.

In addition to this purely scientific output, the technical improvements and our ability to compare PI-GC-AdResS results with those of equilvalent full path integral simulations will greatly expand the diversity of the systems we can study and help us to refine our existing methods even further.

Aim

Our goal is to move towards the use of the PI-GC-AdResS approach to investigate, at the quantum level, the aggregation propsensity of a large system of hydrophobic molecules. In order to achieve this, we will (1) improve the efficiency and accuracy of PI-GC-AdResS by incorporating the ring polymer contraction method and including more precise, detailed path integral water models and (2) develop and refine NEMD methods for PI-GC-AdResS in order to introduce a tunable electric field with which one may modify its frequency and amplitude.

Method

All simulations will be performed using a home-modified version of the molecular dynamics software package GROMACS. All technical improvements to the current PI-GC-AdResS scheme will be implemented and tested using small PI systems. Priority will go to efficiency enhancements such as implementation of ring-contraction PI techniques and accuracy enhancements with testing of numerous PI water models. Following the successful execution of technical improvements, we will then implement the NEMD approach in PI-GC-AdResS and study, as a preliminary test case, an alanine dipeptide solvated in water. We will investigate how the solvation shell structure surrounding the hydrophobic molecule changes as a function of frequency and amplitude of the electric field.

Despite the technical additions planned for PI-GC-AdResS which aim to improve computational efficiency, the cost of the planned simulations is still extremely expensive. Although the GC-AdResS method reduces computational cost, it must still be noted that PIMD techniques in the high-resolution region of these adaptive resolution simulations increase the number of calculations by at least ~32x. In addition to this, NEMD simulations require multiple nearly-identical simulations in order to produce meaningful values of a given quantity of interest. Finally, parallel to each PI-GC-AdRes simulation, an identical full path integral simulation must be performed in order for us to compare our PI-GC-AdResS results. For all simulations, this represents a considerable computational roadblock for our project unless extensive highly-parallel computing resources are available. Thus, we believe that our project will benefit greatly from resources allocated by the HLRN.

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https://userpage.fu-berlin.de/dellesite/

More Information

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