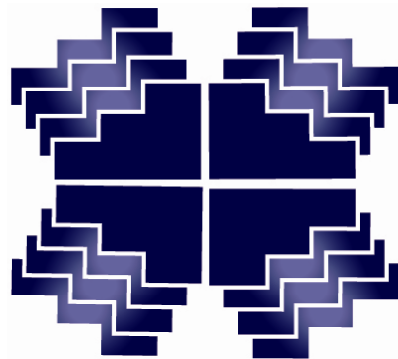


Multiscale Materials Modeling

Lecture 10

Adaptive Resolution



STAIR

Sustainable Technology through
Advanced Interdisciplinary Research

Reminder

In the previous lecture module, we discussed QM/MM as an example of dual scale modeling.

All discussion in that module, assumed that a particle that initially appeared in the finely resolved (primary) subsystem remained in that subsystem for the entirety of the simulation. Similarly, a particle that initially appeared in the coarsely resolved (secondary) subsystem remained in that subsystem for the entirety of the simulation.

In this module, we discuss techniques that allows exchange of particle from one resolution to another during the course of the simulation. This is typically called **adaptive resolution**.

In this lecture module, we review three papers.

- I. “Recent Progress in Adaptive Multiscale Molecular Dynamics Simulation of Soft Matter” S.O. Nielsen, R.E. Buló, P.B. Moore & B. Ensing, *Phys. Chem. Chem. Phys.* **12**(139) 2010 pp. 12401–12414.
- II. “Multiscale Simulation of Soft Matter: From Scale Bridging to Adaptive Resolution”, M. Praprotnik, L. Delle Site & K. Kremer, *Annu. Rev. Phys. Chem.* **59** 2008 pp. 545–71.
- III. “Adaptive Partitioning in Combined Quantum Mechanical and Molecular Mechanical Calculations of Potential Energy Functions for Multiscale Simulations”, A. Heyden, H. Lin & D.G. Truhlar, *J. Phys. Chem. B* **111** 2007 pp. 2231-2241.



PCCP

Physical Chemistry Chemical Physics

www.rsc.org/pccp

Volume 12 | Number 39 | 21 October 2010 | Pages 12329–12876

PERSPECTIVE

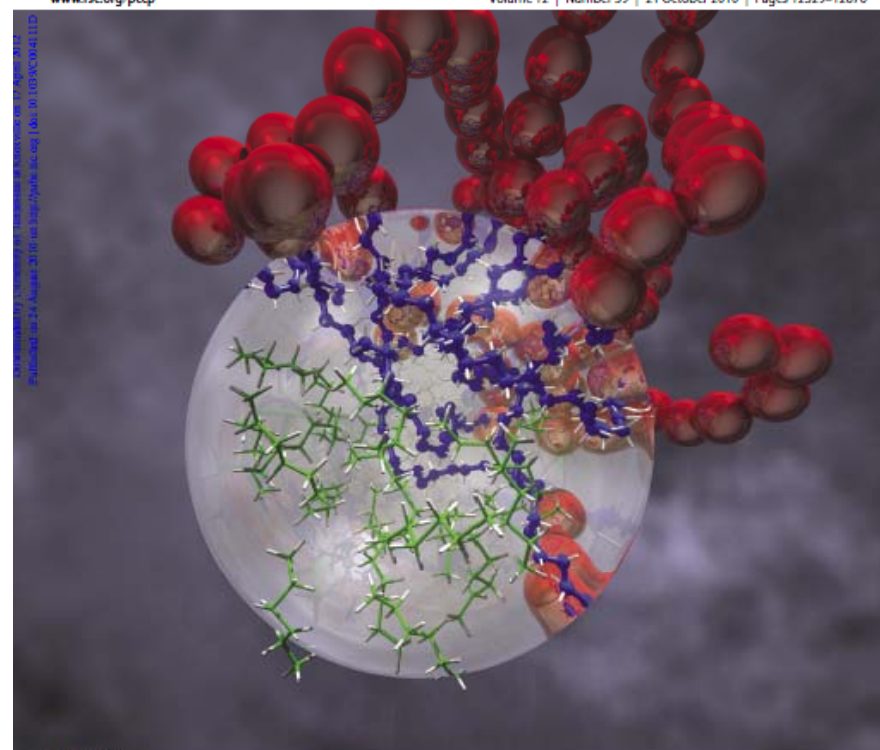
www.rsc.org/pccp | Physical Chemistry Chemical Physics

Recent progress in adaptive multiscale molecular dynamics simulations of soft matter

Steven O. Nielsen,^a Rosa E. Bulo,^b Preston B. Moore^c and Bernd Ensing^{a,d}

Received 10th March 2010, Accepted 3rd August 2010

DOI: 10.1039/c004111d



ISSN 1463-9076

COVER ARTICLE
Ensing et al.
Recent progress in multiscale
molecular dynamics simulation of
soft matter

COMMUNICATION
Zhang et al.
Transverse piezoelectric field-effect
transistor based on single ZnO
nanobelts

Introduction

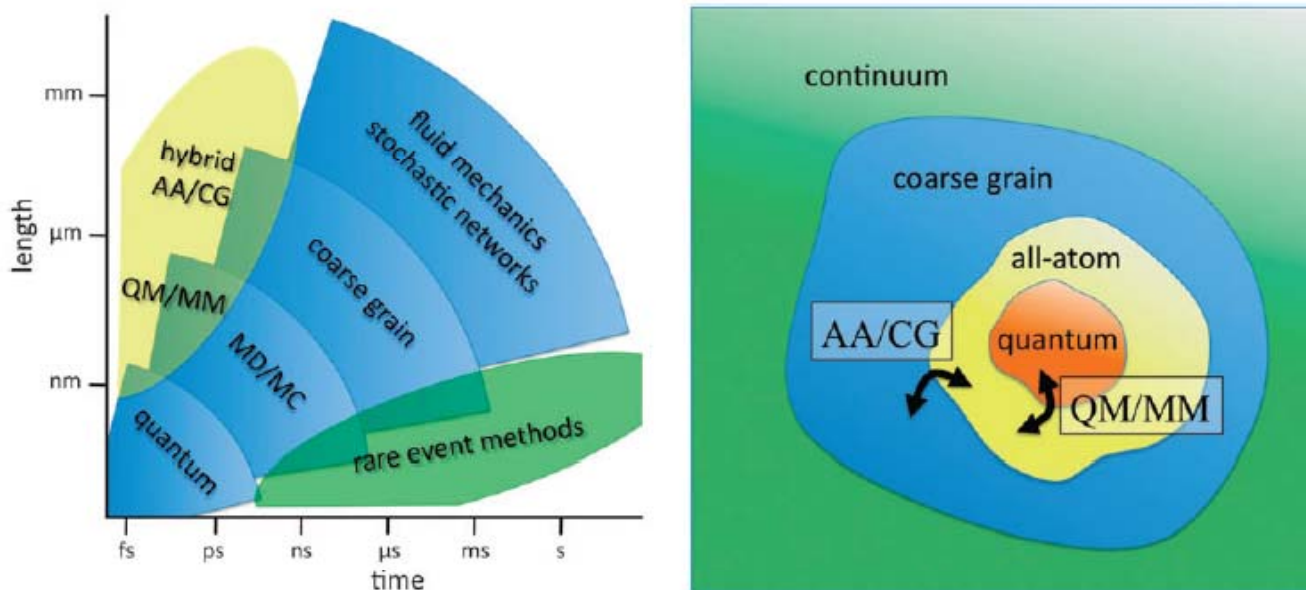


Fig. 1 Left: Schematic graph of the length and time scales accessible to current simulation methods, ranging from highly accurate but computational very demanding *ab initio* molecular dynamics (quantum) in the lower left corner to highly efficient but very low-detail continuum models and stochastic network methods at the top-right corner. In between, we find atomistic molecular dynamics and Monte Carlo simulation followed by coarse-grain molecular dynamics. Advanced sampling methods, so-called rare event techniques, allow for sampling of slow processes on long time scales. Hybrid multiscale methods allow us to move off-diagonal in the direction of large length scales. Right: Illustration of a spatial partitioning of the system in which a hypothetical hybrid model combines four levels of theory. Perhaps the future of hybrid multiscale modeling? Here we focus on hybrid MD methods that combine two levels of resolution, AA/CG and QM/MM, in which molecules can dynamically change their level of resolution by diffusing across the resolution boundaries.

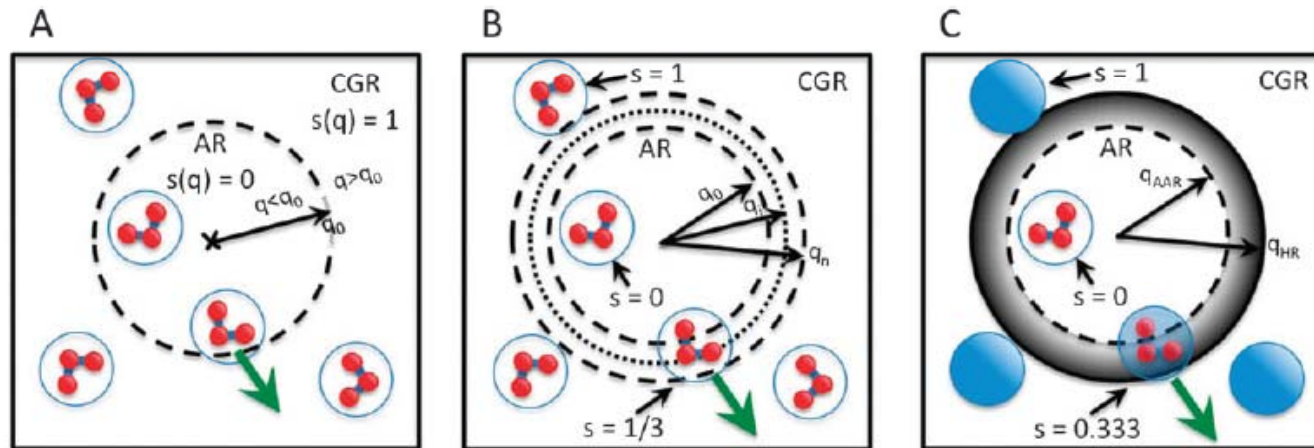
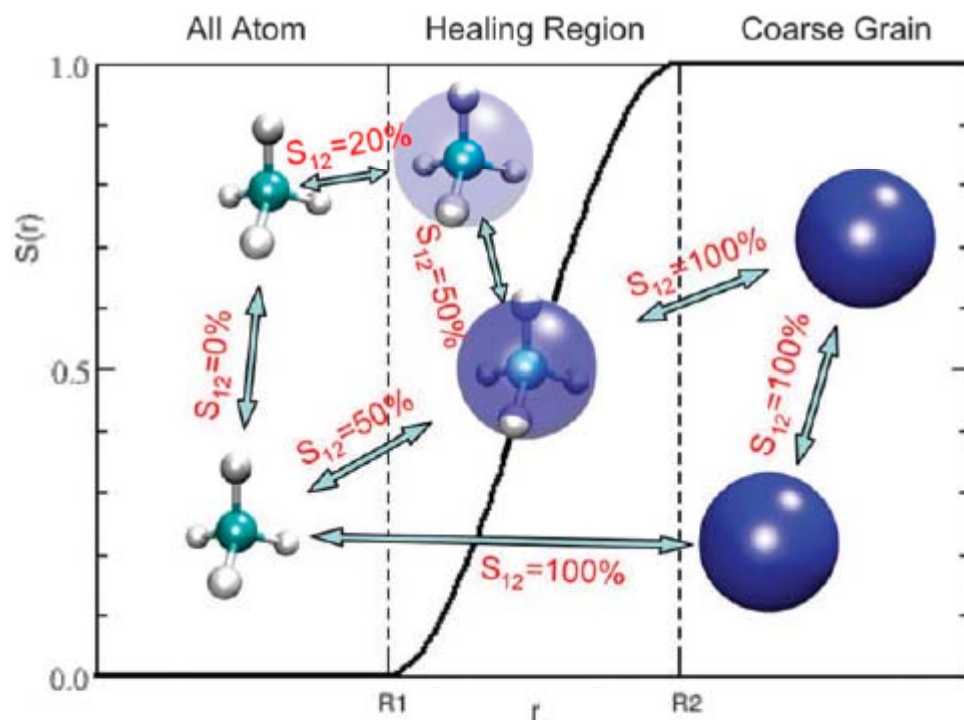


Fig. 2 Introduction of the hand-shaking healing region that couples the atomistic region (AR) with the coarse-grain region (CGR). Panel A: an order parameter q partitions the system into an AR where the particles carry a label $s = 0$ and a CGR where $s = 1$. Panel B: Intermediate regions are inserted where hybrid particles carry intermediate s values so that jumps in the potential energy due to particles crossing region boundaries are split into smaller steps. Panel C: by assuming an infinite number of intermediate regions a smooth transition region is established. In the CGR the groups of atoms are frozen and replaced by CG sites.

The “hand-shaking” or “healing” region separates the finely resolved from the coarsely resolved systems. A weighting function is used to assign a fractional resolution to particles in the HR depending upon their spatial location.

Application to Methane



Example of methane from all atom to united atom representation.

Fig. 3 Schematic representation of methane in the atomistic region (at the left), the coarse-grain region (at the right), and the connecting healing region (in the middle). The solid black line shows the value of the switching function for a CG site as a function of its position, $s(r)$. The scaling (λ) of each pair interaction equals the maximum $s(r)$ among the two interacting CG sites (indicated in red). Figure taken from ref. 48.

Application to Methane

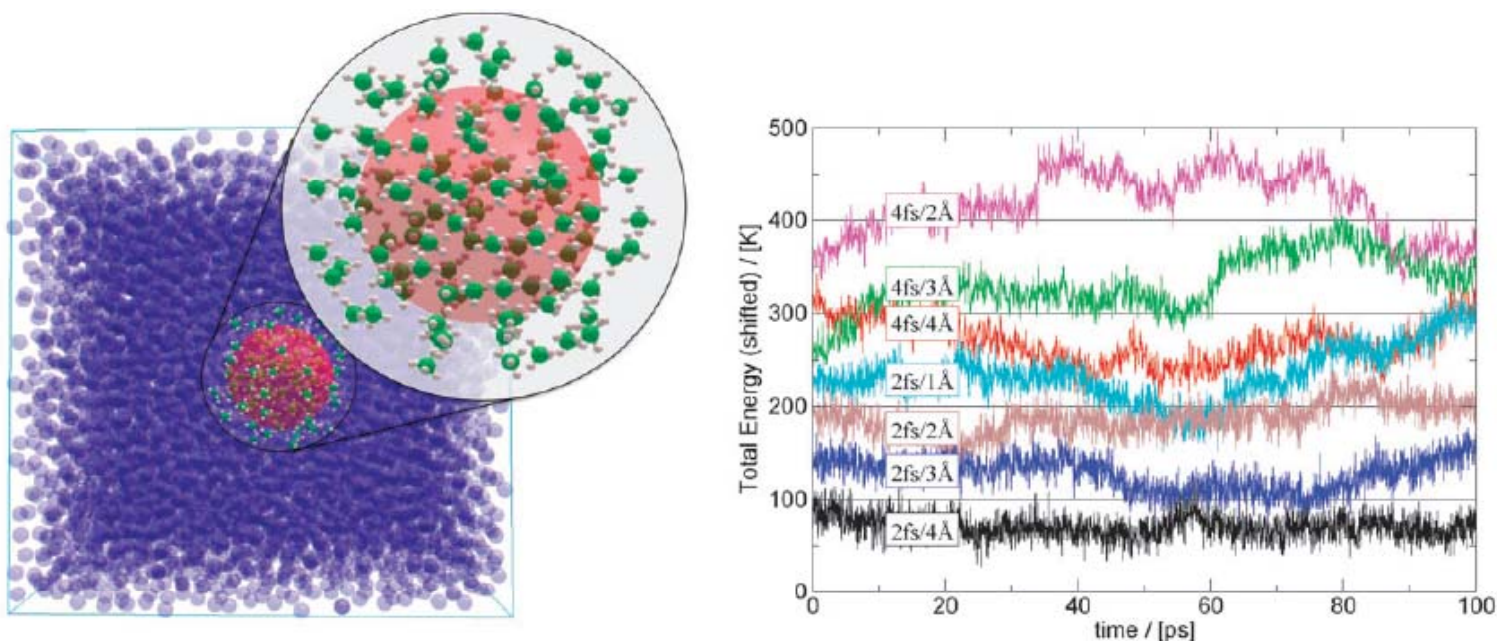


Fig. 4 Snapshot of the hybrid MD simulation of liquid methane (left). The inset zooms in onto the spherical atomistic region, indicated by the red sphere, and the surrounding healing region. The CG united-atom resolution (blue spheres) is omitted from the inset for clarity. At the right: total energy for seven separate hybrid MD simulations with varying time steps and healing region widths. A too large time step or too narrow HR results in poor energy conservation. Graph taken from ref. 38.

All atoms particles carry more kinetic energy than united atom particles (think of the vibrational energy of bonds absent in UA descriptions). Thus various techniques are devised to artificially maintain energy conservation.

Application to solvated polymers

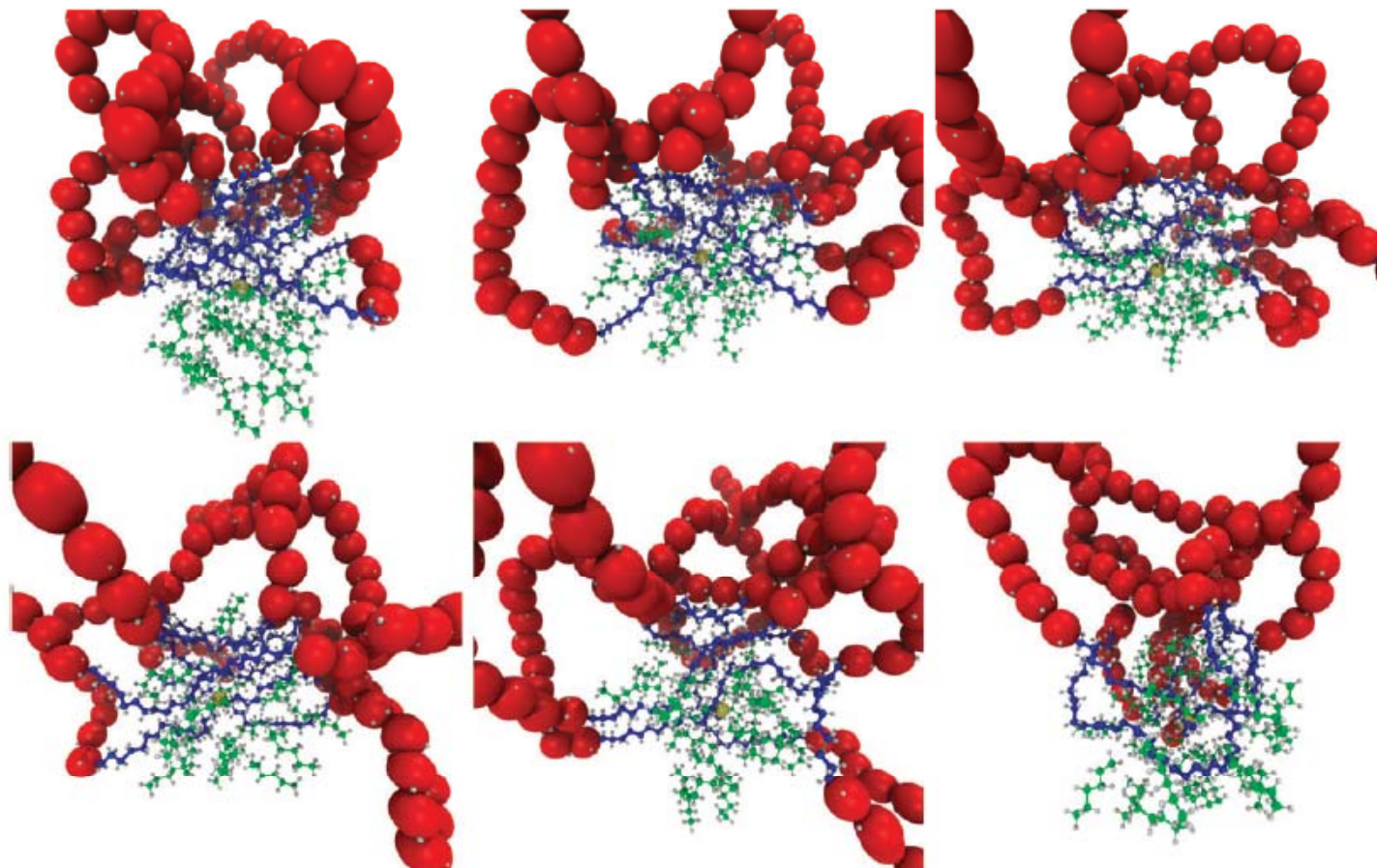


Fig. 7 Six snapshots taken at $t = 0, 50, 100, 150, 200$ and 400 ps, from an adaptive hybrid AA/CG simulation of the solvation and unfolding of a polyethylene chain in hexane. A spherical atomistic region is centered halfway along the chain (the center is indicated by a yellow sphere). In the CGR the chain is represented by red spheres. In the AR and HR the chain is shown in blue and white balls and sticks. The penetrating hexane molecules are shown in the green and white ball and stick representation in the AR and the HR; in the CGR the hexane solvent is omitted for clarity.

Adaptive QM/MM example

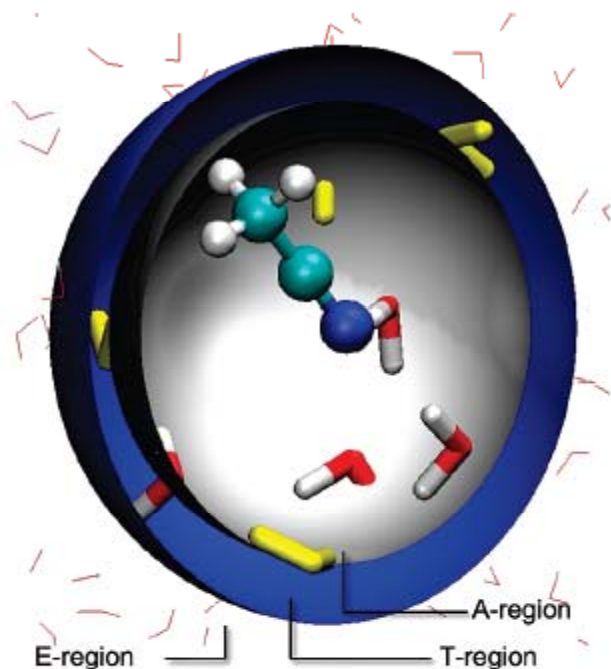
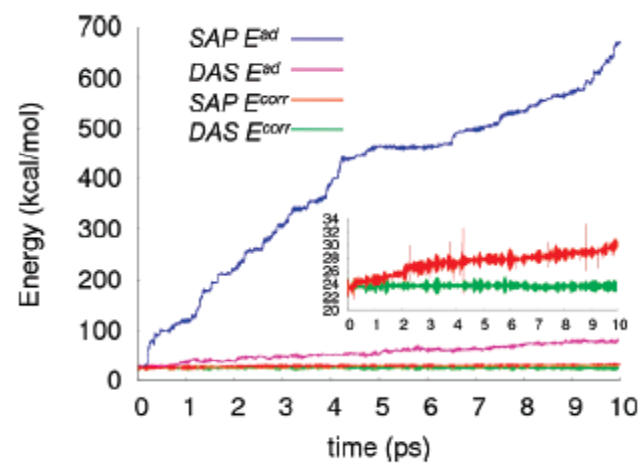


Figure 9. Division of the acetonitrile in water system for adaptive QM/MM.



Analogous techniques can also be applied to QM/MM systems. Here, water molecules can move in and out of the QM region. The papers are largely about method validation (energy conservation) rather than new science.

Multiscale Simulation of Soft Matter: From Scale Bridging to Adaptive Resolution

Matej Praprotnik,* Luigi Delle Site,
and Kurt Kremer

Max-Planck-Institut für Polymerforschung, D-55128 Mainz, Germany;
email: praprot@mpip-mainz.mpg.de, dellsite@mpip-mainz.mpg.de,
kremer@mpip-mainz.mpg.de

This paper gives a very similar description to the adaptive resolution problem from a different research group.

Paper 2. Adaptive AA/CG

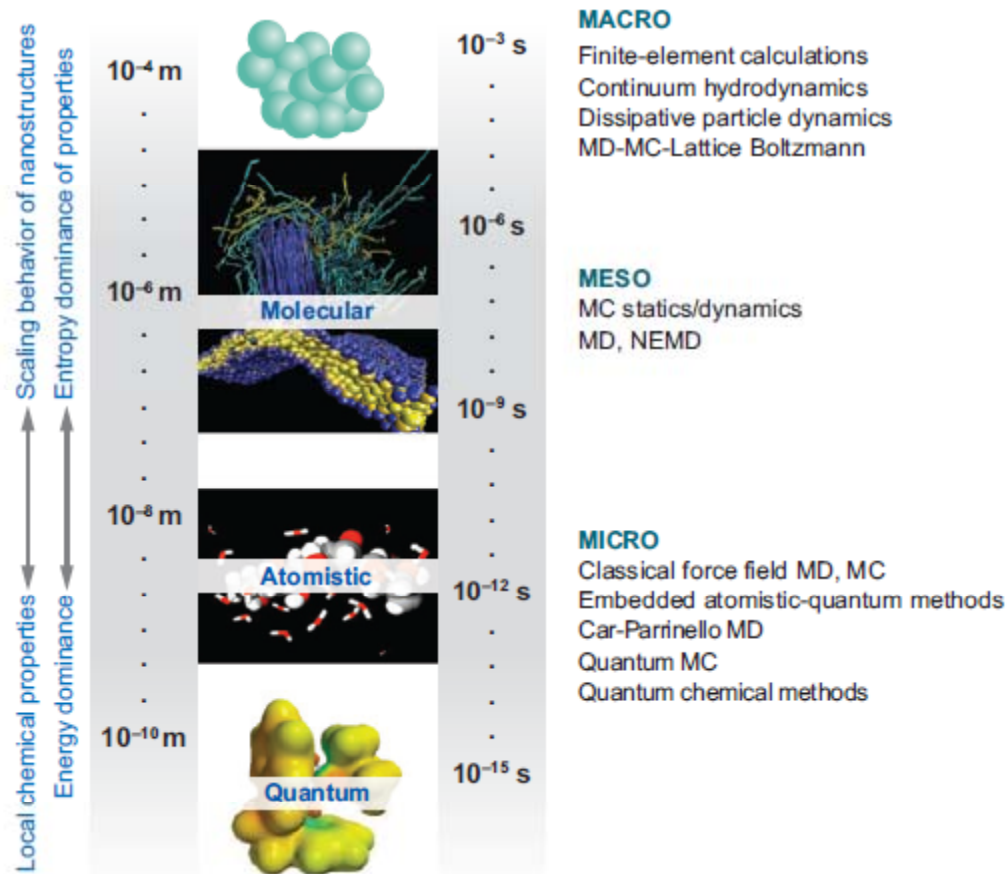


Figure 1

Illustration of the different length and time scales relevant for the simulation of soft matter. Here we deal with the lower three levels of resolution, which all introduce features that carry through into the macroscopic properties of the systems. We show only a selection of representative methods employed at each scale. MC, Monte Carlo; MD, molecular dynamics; NEMD, nonequilibrium molecular dynamics.

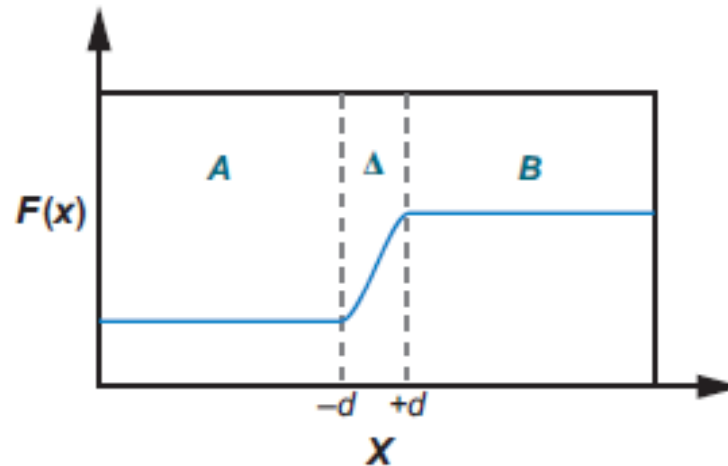


Figure 5

The free energy F associated with DOFs explicitly considered in a simulation as a function of x . A and B are the regions with low and high levels of detail, respectively, whereas Δ is a transition regime. The constant values of F_A and F_B are arbitrary and do not play any role in the following treatment.

Drive to establish multiscale modeling as a thermodynamic equilibrium between different species.

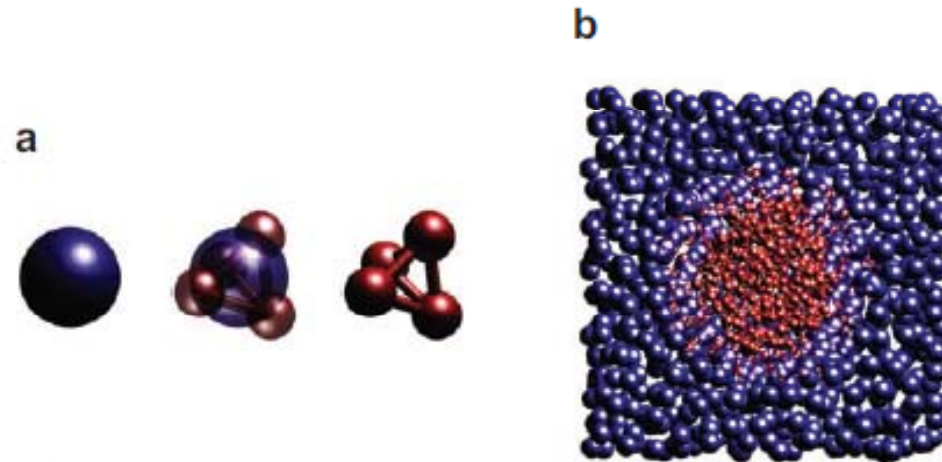


Figure 6

(a) The on-the-fly interchange between the atomistic (*far-right molecule*) and coarse-grained (*far-left molecule*) levels of description. The middle hybrid molecule is a linear combination of a fully atomistic molecule with an additional center-of-mass particle representing the coarse-grained molecule. (b) Snapshot of the hybrid atomistic/mesoscopic model liquid with $\rho = 0.175$ and $T = 1.0$. The red molecules are the explicit atomistically resolved tetrahedral molecules, and the blue molecules are the corresponding one-particle coarse-grained molecules.

Again, a transition region is introduced which uses weighting functions to shift from one resolution to the other.

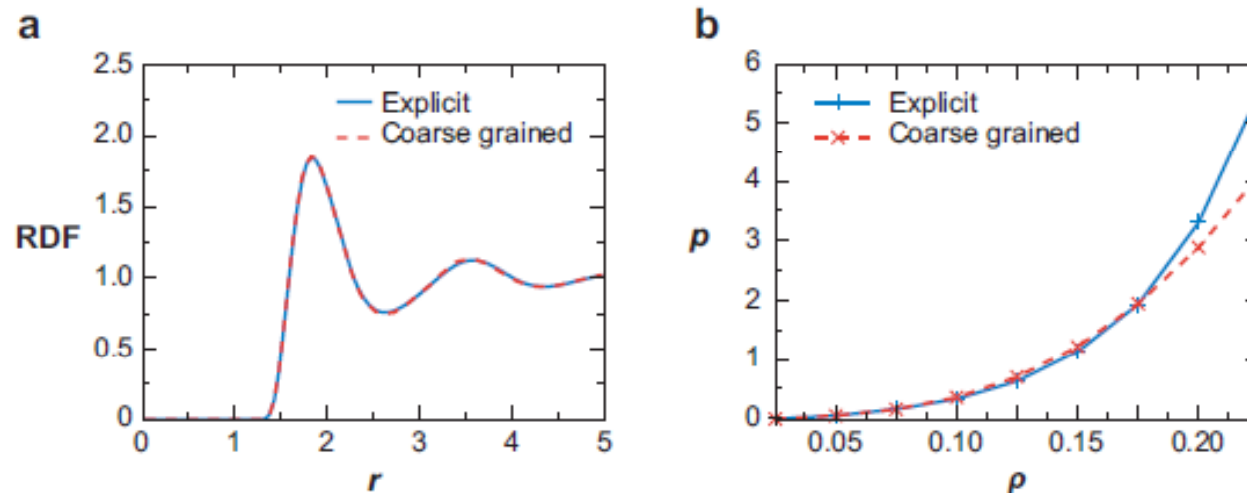


Figure 7

(a) The center-of-mass radial distribution function (RDF_{cm}) of the explicit and coarse-grained systems at $T = 1$ and $\rho = 0.175$. The two RDF_{cm} s match to the line thickness. (b) Equation of state for the explicit and coarse-grained systems at $T = 1$ and $\rho = 0.175$. Shown is the pressure p as a function of the number density ρ of the system. The equations of state coincide around the state points for which the effective potentials were parameterized. Figure adapted from Reference 13.

Validation involves reproducing the pair correlation function for both levels of resolution.

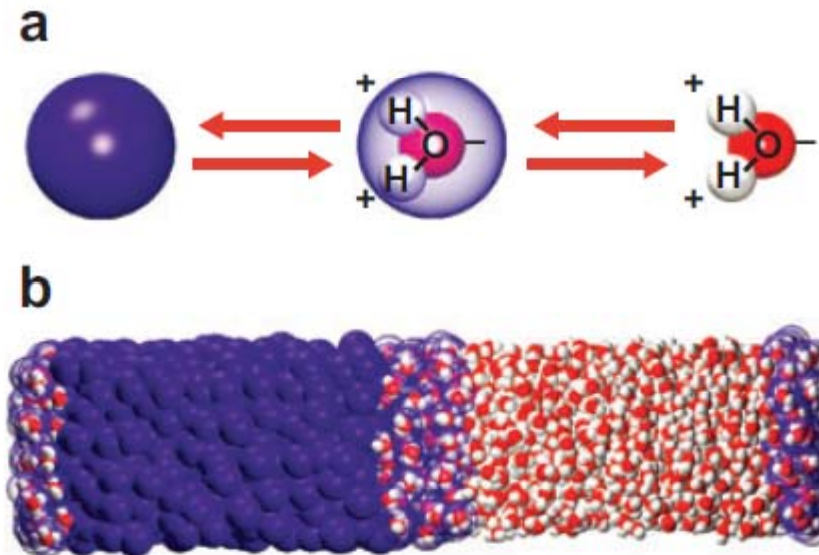


Figure 11

(a) On-the-fly interchange between the all-atom and coarse-grained water models. (b) A schematic representation of the hybrid liquid-water system.

Validation involves reproducing the pair correlation function for both levels of resolution.

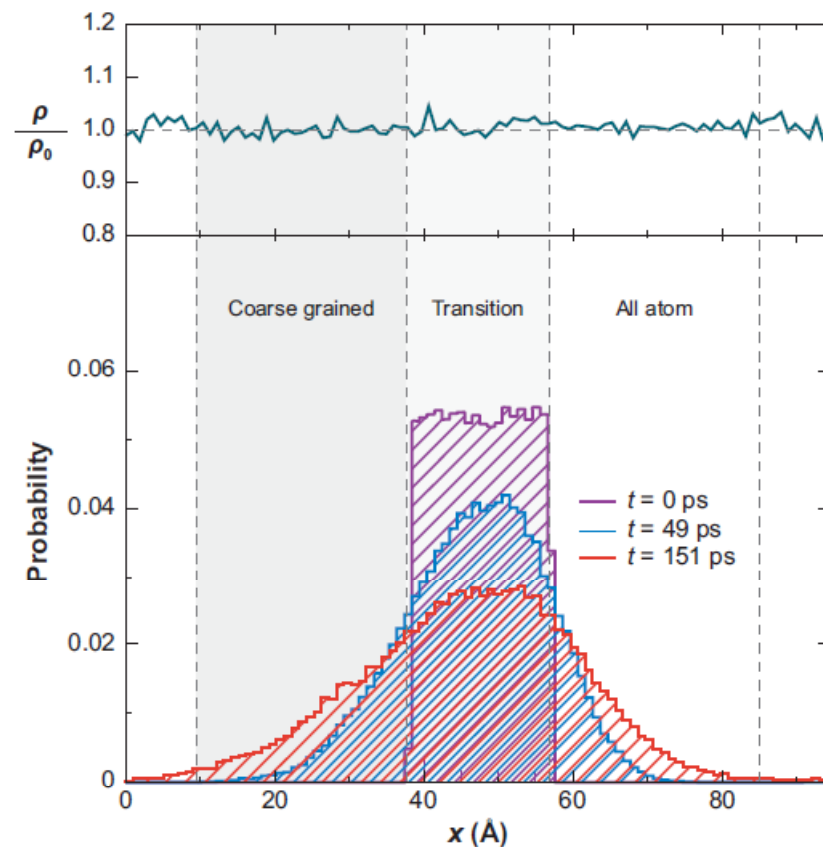


Figure 13

(*Top panel*) Normalized density profile in the x direction of the hybrid system. (*Bottom panel*) Time evolution of a diffusion profile for the molecules that are initially (at time $t = 0$ ps) located in the interface region. The diffusion profile is averaged over ≈ 400 different time origins. Vertical lines denote the boundaries of the interface layer. Figure taken from Reference 75.

Diffusion is asymmetric in this system because the diffusion coefficients of the all-atom molecules are different than the CG particles.

Details of the techniques are still being improved

PRL 107, 099801 (2011)

PHYSICAL REVIEW LETTERS

week ending
26 AUGUST 2011

Comment on “Adaptive Multiscale Molecular Dynamics of Macromolecular Fluids”

In a recent Letter, Nielsen, Moore, and Ensing [1] presented an “energy-conserving” adaptive resolution method for coupling different molecular representations. We here comment only on their basic simulation concept. We show that the algorithm, as described in the text, does not conserve thermodynamic equilibrium and will produce a significant energy drift. To couple an atomistic and

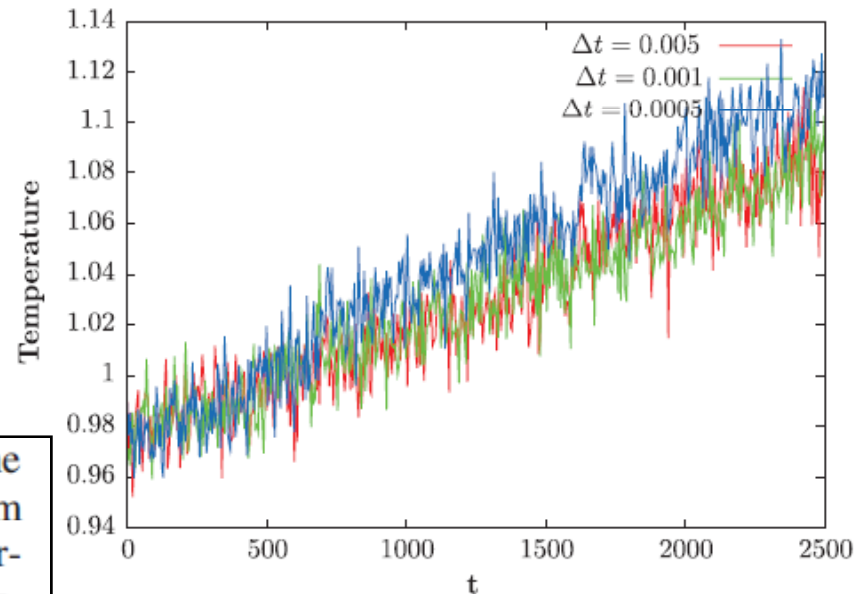


Fig. 1 (color). Temperature as a function of time for different integration time steps, in reduced units as in Ref. [2].

In contrast, as shown for the adaptive resolution scheme method [2] (Ref. [9] of [1]), thermodynamic equilibrium can be controlled *only* by coupling the system to an external field and/or to a local thermostat [7]. That the “book-keeping energy” is meaningless was stated already by other authors [8]. For the case where DOFs also must be reinserted (or removed) in the healing region, the extra heat given by the thermostat for this process can be quantified *a posteriori* via the concept of fractional DOFs [7]. Moreover, the role of the thermostat as the only crucial tool to reintroduce DOFs has been clearly demonstrated in Ref. [9], where the reduction (or reinsertion) of 117 DOFs per molecule was performed.

J. Phys. Chem. B 2007, 111, 2231–2241

2231

Adaptive Partitioning in Combined Quantum Mechanical and Molecular Mechanical Calculations of Potential Energy Functions for Multiscale Simulations

Andreas Heyden,^{*,†} Hai Lin,[‡] and Donald G. Truhlar^{*,†}

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, and Department of Chemistry, University of Colorado at Denver and Health Science Center, Denver, Colorado 80217-3364

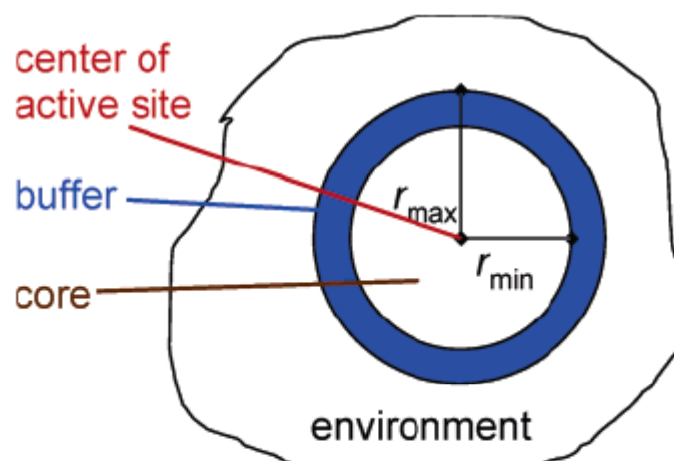


Figure 1. Partitioning of a multilevel system into an active (core) zone, buffer zone, and environmental zone.

A similar view as the first paper. Different terminology for the three regions. Core is QM. Environment is MM or lower level QM.

$$V = V^{\text{entire}}(\text{MM}) + (V^{\text{A+B}}(\text{QM}) - V^{\text{A+B}}(\text{MM})) \quad (1)$$

$$\mathbf{f}_i = \mathbf{f}_i^{\text{entire}}(\text{MM}) + S(r_i)(\mathbf{f}_i^{\text{A+B}}(\text{QM}) - \mathbf{f}_i^{\text{A+B}}(\text{MM})) \quad (2)$$

where $V^{\text{entire}}(\text{MM})$ is the potential energy of the entire system calculated at the low level of theory and $V^{\text{A+B}}(\text{QM})$ and $V^{\text{A+B}}(\text{MM})$ are the potential energies of all groups in the active (A) and buffer (B) zones treated at the high and low level of theory, respectively. The zero of energy is defined for both levels

Energy and forces are computed at both QM and MM levels in the core and buffer regions. A switching function is used to switch between them.

$$S(r_i) = \begin{cases} 1 & \text{for } r_i \leq r_{\min} \\ \frac{(r_{\max}^2 - r_i^2)^2(r_{\max}^2 + 2r_i^2 - 3r_{\min}^2)}{(r_{\max}^2 - r_{\min}^2)^3} & \text{for } r_{\min} < r_i < r_{\max} \\ 0 & \text{for } r_i \geq r_{\max} \end{cases} \quad (3)$$

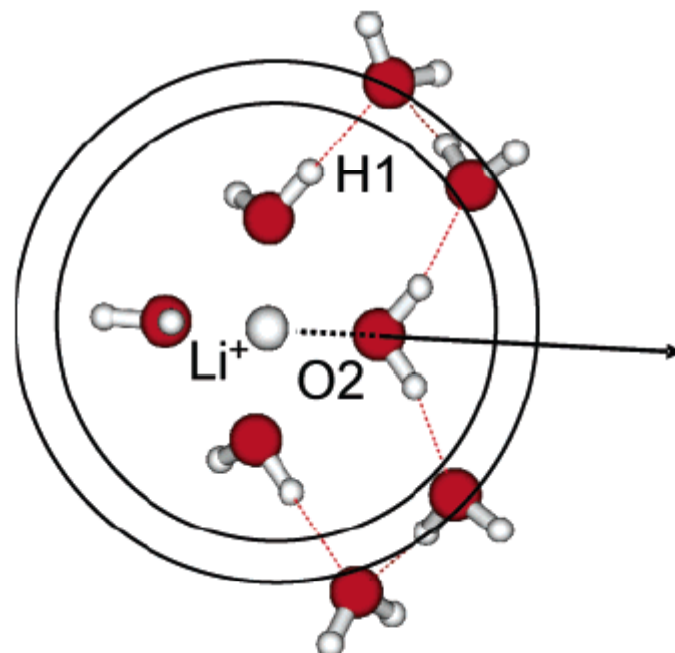


Figure 3. Initial configuration for the simulation of a Li^+ atom surrounded by a water cluster. The system is partitioned into an active zone with initially four water molecules, a buffer zone with initially two water molecules, and an environmental zone with initially two water molecules. The arrow illustrates the movement of the water molecule leaving the first solvation shell of the Li^+ atom.

This example studies solvation around a Lithium ion.

Energy and Forces

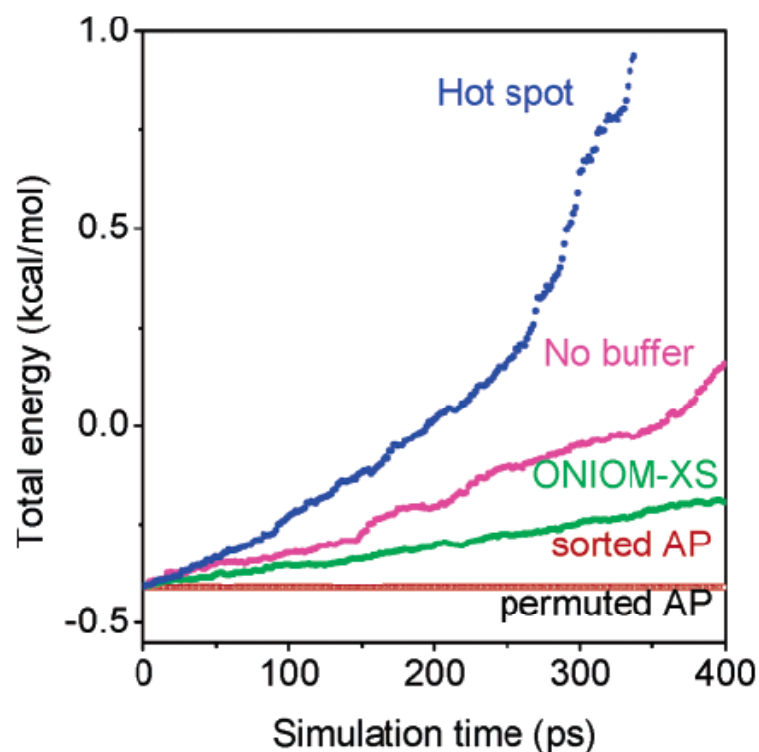


Figure 7. Total energy during an MD simulation in the microcanonical ensemble. The system consists of 171 argon atoms in a periodic box with a box length of 20 Å. One atom is chosen to be the primary group, and the radius of the active zone is $r_{\min} = 5$ Å. Trajectories are computed using the hot spot, ONIOM-XS, permuted AP, and sorted AP methods with a buffer zone 0.5 Å thick and also a scheme with an infinitesimally narrow buffer zone ($r_{\min} = r_{\max} = 5.5$ Å). Total energy data from the simulation using the permuted AP method are directly underneath the data from the sorted AP simulation.

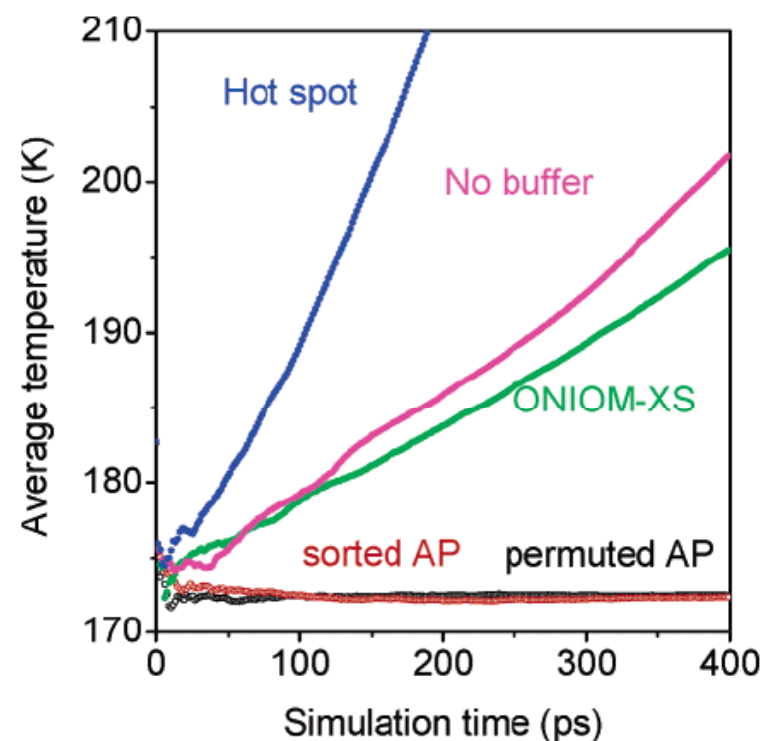


Figure 8. Average temperature during an MD simulation in the microcanonical ensemble. (The average is performed from the beginning of the simulation to time t .) The system consists of 171 argon atoms in a periodic box with a box length of 20 Å. One atom is chosen to be the primary group, and the radius of the active zone is $r_{\min} = 5$ Å. Trajectories are computed using the hot spot, ONIOM-XS, permuted AP, and sorted AP methods with a buffer zone 0.5 Å thick and also a scheme with an infinitesimally narrow buffer zone ($r_{\min} = r_{\max} = 5.5$ Å).

Again, energy conservation is the standard for validation of the technique.

Conclusions

Adaptive Resolution techniques exist to simulate dual resolution models in which particles can exchange between levels of resolution.

These models employ switching functions to transition from AA to CG or from QM to MM.

Care must be taken to ensure stability (energy conservation of the system).

Validation is based on reproducing some property of the more finely resolved system (such as the pair correlation function).

Approaches are still being fine-tuned.

There remain issues such as the asymmetry of diffusion, which has yet to be resolved.