Adaptive Resolution Molecular Dynamics Simulation (AdResS): Changing the Degrees of Freedom on the Fly

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Motivations

• many problems in the condensed matter are inherently multiscale
• interplay between different length scales plays the crucial role in the physics of the system
• an exhaustive description of the system requires the simultaneous treatment of all the relevant scales implied
• the aim is to treat in a simulation only as many degrees of freedom as absolutely necessary for the problem considered
• some regions require a treatment on a higher level of detail than the remainder of the system
**MD simulation**

**All-Atom MD simulation:**
- allows to study processes at the atomic level of detail
- is often incapable to bridge a gap between a wide range of length and time scales involved in the complex molecular systems

**Coarse-Grained MD simulation:**
- reduces the number of degrees of freedom by retaining only those degrees of freedom that are relevant for the particular property of interest \( \Rightarrow \) longer length and time scales can be reached
- specific chemical details are usually lost in the coarse-graining procedure

**Solution:**
- Hybrid Adaptive MD Schemes
Example I: Solvation of Complex Molecules
Example II: Large Molecules near Inorganic Surfaces
Method and model: general idea

Adaptive Resolution MD Scheme

- allows an on-the-fly interchange between given molecule’s atomic and coarse-grained levels of description, i.e., changing the molecular degrees of freedom

Hybrid Model

with: $\mu_{ex} = \mu_{cg}$, $p_{ex} = p_{cg}$, $T_{ex} = T_{cg}$
Theoretical basis of the idea: A simple schematic picture

Simple schematic picture

- A and B are **physically identical** but **differently represented**
- For B the only assumption (tested numerically) is that for a state point \((\rho, T)\) it is possible to reduce the many body potential of the high resolution description to a dimensionally reduced effective potential.
Theoretical basis

Question to address: What are the basic statistical principles governing the changing of DOF?

- The passage from $A$ to $B$ can be thought as a geometrically induced phase transition, i.e. formally equivalent to a standard phase transition.

- The equivalent of the latent heat is the energy one must give to or take from the molecules depending on the fact that the molecules acquire or loose DOF.

- In a simulation this would mean the use of a THERMOSTAT.
The theoretical basis involves the transition region. Let's examine what happens in the infinitesimal region at the interface between A and B.

- The number of DOF is $n = n(x)$ with $n_A = \text{const}_A$; $n_B = \text{const}_B$; and $n_{\Delta} = n(x)$.

- The system is in equilibrium which implies:
  \[
  \lim_{x \to d^{-}} \frac{\partial F_A(x)}{\partial x} = \lim_{x \to d^{+}} \frac{\partial F_B(x)}{\partial x} = 0
  \]

- If the condition above did not hold, a molecule would 'see' a free energy density gradient along $x$ within the same level of resolution leading to a drift along the $x$ axis.
Theoretical Basis: Weighting function

- \( \lim_{x \to d^-} \frac{\partial F_A(x)}{\partial x} = \lim_{x \to d^+} \frac{\partial F_B(x)}{\partial x} = 0 \) can be shown to be equivalent to
  \( \lim_{x \to d^-} \frac{\partial n_A(x)}{\partial x} = \lim_{x \to d^+} \frac{\partial n_B(x)}{\partial x} = 0 \)

- This suggests that we can formally describe the switching on/off of a given DOF via a weighting function \( w(x) \)

- \( w(x) \) is such that \( w(x) = 1; \forall x \in A \) and \( w(x) = 0; \forall x \in B \), with
  \( \lim_{x \to d^+} \frac{\partial w(x)}{\partial x} = \lim_{x \to d^-} \frac{\partial w(x)}{\partial x} = 0. \)

- In accordance with the equation above, we require that the weighting function \( w(x) \) be continuous up to the first derivative and that goes monotonically from the value one to zero in the region \( \Delta \).
Temperature in the region \( \Delta \)

- According to the **Equipartition Theorem** \( T_A = 2 \frac{\langle K_A \rangle}{n_A} \); \( T_B = 2 \frac{\langle K_B \rangle}{n_B} \)

- but in \( \Delta \), is \( T_\Delta = 2 \frac{\langle K_\Delta \rangle}{n_\Delta} \)? And what is \( \langle K_\Delta \rangle \)?

- We must know \( T_\Delta \) to control it and to avoid kinetic barriers.
Switching resolution and the fractional dimensions of the phase space

- The switching procedure implies that in the transition regime, where $0 < w(x) < 1$, we deal with fractional DOFs, i.e., by switching on/off a DOF we continuously change the dimensionality of the phase space.

- To properly describe this situation we resort here to the fractional calculus.

- By this have derived the fractional analog of the equipartition theorem:
  \[ \langle K_\alpha \rangle = \frac{\alpha}{2\beta} = \frac{\alpha T}{2}. \]
  where $\langle K_\alpha \rangle$ is the average kinetic energy per fractional DOF with $\alpha$ degree of fractionality.
Theoretical Basis: Conclusions

• (1) Changing Resolution formally equivalent to a Phase Transition $\rightarrow$ Latent Heat

• (2) At the interface it is required the introduction of a switching region, $\Delta$, and a related function, $w(x)$, to allow for a smooth variation of the resolution

• (3) The temperature in the switching region, $T_\Delta$, can be obtained by extending the equipartition theorem to non integer dimensions


• Still to address for a practical MD algorithm: How to express the interactions between molecules.
Adaptive Resolution Scheme

The Adaptive resolution scheme scheme is a two-stage procedure:

- Derive the effective pair potential $U^{cm}$ between coarse-grained molecules on the basis of the reference all-atom system.

- Couple the atomistic and mesoscopic scales:

$$F_{\alpha \beta} = w(X_\alpha)w(X_\beta)F_{\alpha \beta}^{atom} + [1 - w(X_\alpha)w(X_\beta)]F_{\alpha \beta}^{cm},$$

where:

$$F_{\alpha \beta}^{atom} = \sum_{i_\alpha, j_\beta} F_{i_\alpha j_\beta}^{atom}$$

is the sum of all pair interactions between explicit atoms of molecules $\alpha$ and $\beta$

and

$$F_{i_\alpha j_\beta}^{atom} = -\frac{\partial U_{atom}}{\partial r_{i_\alpha j_\beta}},$$

$$F_{\alpha \beta}^{cm} = -\frac{\partial U^{cm}}{\partial R_{\alpha \beta}}.$$
Weighting Function

where $a$ is the box length and $d$ the half-width of the interface layer.
Interactions

Shifted 12-6 Lennard-Jones potential:

\[ U_{atom}^{LJ}(r_{i\alpha j\beta}) = \left\{ \begin{array}{ll}
4\varepsilon \left[ \left( \frac{\sigma}{r_{i\alpha j\beta}} \right)^{12} - \left( \frac{\sigma}{r_{i\alpha j\beta}} \right)^{6} + \frac{1}{4} \right]; & r_{i\alpha j\beta} \leq 2^{1/6}\sigma \\
0; & r_{i\alpha j\beta} > 2^{1/6}\sigma
\end{array} \right. \]

FENE potential:

\[ U_{atom}^{FENE}(r_{i\alpha j\alpha}) = \left\{ \begin{array}{ll}
-\frac{1}{2}kR_{0}^{2}\ln\left[ 1 - \left( \frac{r_{i\alpha j\alpha}}{R_{0}} \right)^{2} \right]; & r_{i\alpha j\alpha} \leq R_{0} \\
\infty; & r_{i\alpha j\alpha} > R_{0}
\end{array} \right. \]
Coupling the atomistic and mesoscopic scales via a POTENTIAL approach

- One could, in principle, also define the coupling scheme using the respective potentials instead of forces as:
  \[ U_{\alpha\beta} = w(x_\alpha)w(x_\beta)U_{\alpha\beta}^{atom} + [1 - w(x_\alpha)w(x_\beta)]U_{\alpha\beta}^{cg} \]

- A force defined as a gradient of this potential would not obey Newton’s Third Law unless,
  \[ \frac{1}{w(x_\alpha)} \frac{\partial w(x_\alpha)}{\partial x_\alpha} = - \frac{1}{w(x_\beta)} \frac{\partial w(x_\beta)}{\partial x_\beta} \]
  i.e. \( w(x_\alpha) = w(x_\beta) = const \)

- In general, the existence in mathematical terms of a proper (generic) switching function for potentials is a serious problem.
Results for a medium dense liquid

Global and local structure are properly reproduced
Number of DOFs

\[ n_{DOS} = 3n[4w + (1 - w)] \]

Numerical proof of the "Zero Flux"
Diffusion across the transition regime

(e) Coarse-grained side.

(f) Explicit side.

Dense Liquid

Spherical Symmetry:

\[ \mathbf{F}_{\alpha\beta} = w(R_{\alpha})w(R_{\beta})\mathbf{F}_{\alpha\beta}^{\text{atom}} + [1 - w(R_{\alpha})w(R_{\beta})]\mathbf{F}_{\alpha\beta}^{\text{cm}}, \]
Tabulated effective pair potential

(i) Tabulated potential.

(j) RDF<sub>cm</sub>. 
(k) Equation of state for $\rho = 0.175$ and $T = 1$.

(l) RDF$_{cm}$.

Conclusions

Hybrid method (AdResS) for MD simulation:

- Allows for a dynamical switching of the spatial resolution.
- The number of DOFs is changing on-the-fly.
- We treat only as many DOFs as absolutely necessary for the problem considered.
- Method successfully reproduces statistical properties of the model liquid.
Further application: Solvating a Polymer

A generic Polymer solvated by a Tetrahedron Liquid

In collaboration with C.Clementi Group at Rice University.
Projects in progress

- Development of the algorithm for switching large molecules, e.g. polymers, where part of the molecule remains atomistic and part coarse-grained.

- Polymer systems, melts and solution, on specific inorganic surfaces.

Projects of: Simon Poblete and Christoph Junghans
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