Stochastic thermostats

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Problems in molecular simulations (FB810)

NVE ensemble gives the correct dynamics

Experiments work at constant temp so NVT ensemble has to be incorporated

For NVT, we alter the newtons motion to reach the target temperature

The velocity is altered in the system, it changes the dynamic properties and does not give the true result

Thermostat → Constant Temperature → Kinetic energy

↓

Equation of motion ← Velocity

$$m_i \frac{d^2r}{dt} = F_i(r_i)$$ → Changing the equation of motion

PROBLEM

Changes in velocity by altering the newton's equation of motion

Dampening of dynamic properties

Deviation from "true" dynamics

Types of thermostats

- Velocity Randomizing
- Velocity rescaling

COUPLING CONSTANT

τ_t (coupling constant) determines how strongly the system is coupled to heat bath

More strongly coupled, $\tau_t \rightarrow 0$
Less strongly coupled, $\tau_t \rightarrow \infty$

Velocity randomizing thermostat

Andersen

randomly reassigning new velocities to a group of molecules

Massive Andersen

randomly reassigning new velocities to all the molecules

Langevin Dynamics

changing the Newtonian equation of motion by adding a frictional term and a random term for collision of molecules

Velocity rescaling thermostat

- **Berendsen**
  - Temperature relaxation is exponential
- **Stochastic rescaling**
  - Temperature relaxation is exponential with correct energy distribution by addition of properly chosen stochastic factor that rescales the kinetic energy
- **Nośe-Hoover**
  - Temperature relaxation in oscillatory manner

Some dynamical properties

Short time scale dynamical properties

- Diffusivity
- Rotational correlation time
- Viscosity

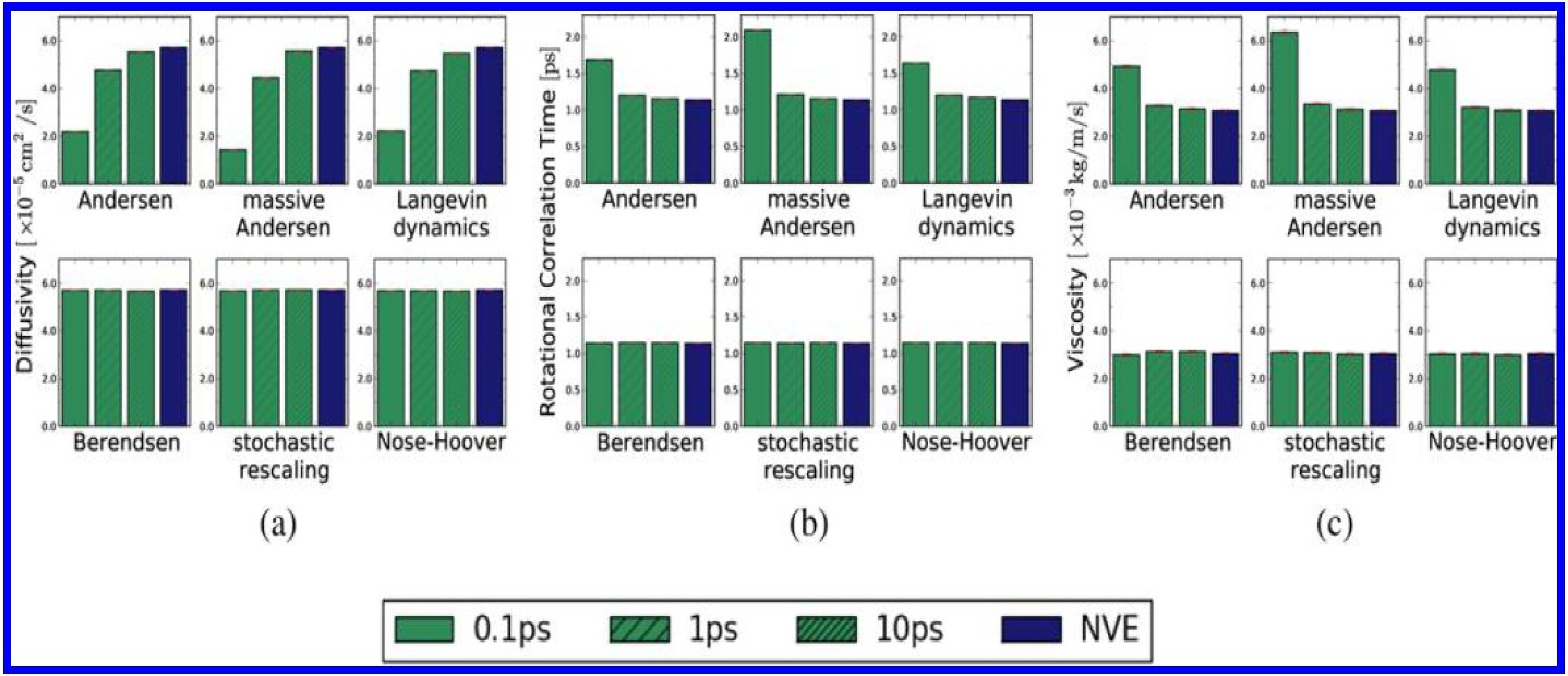
Long time scale dynamical properties

- Dynamic structure factor using Dynamic light scattering experiments

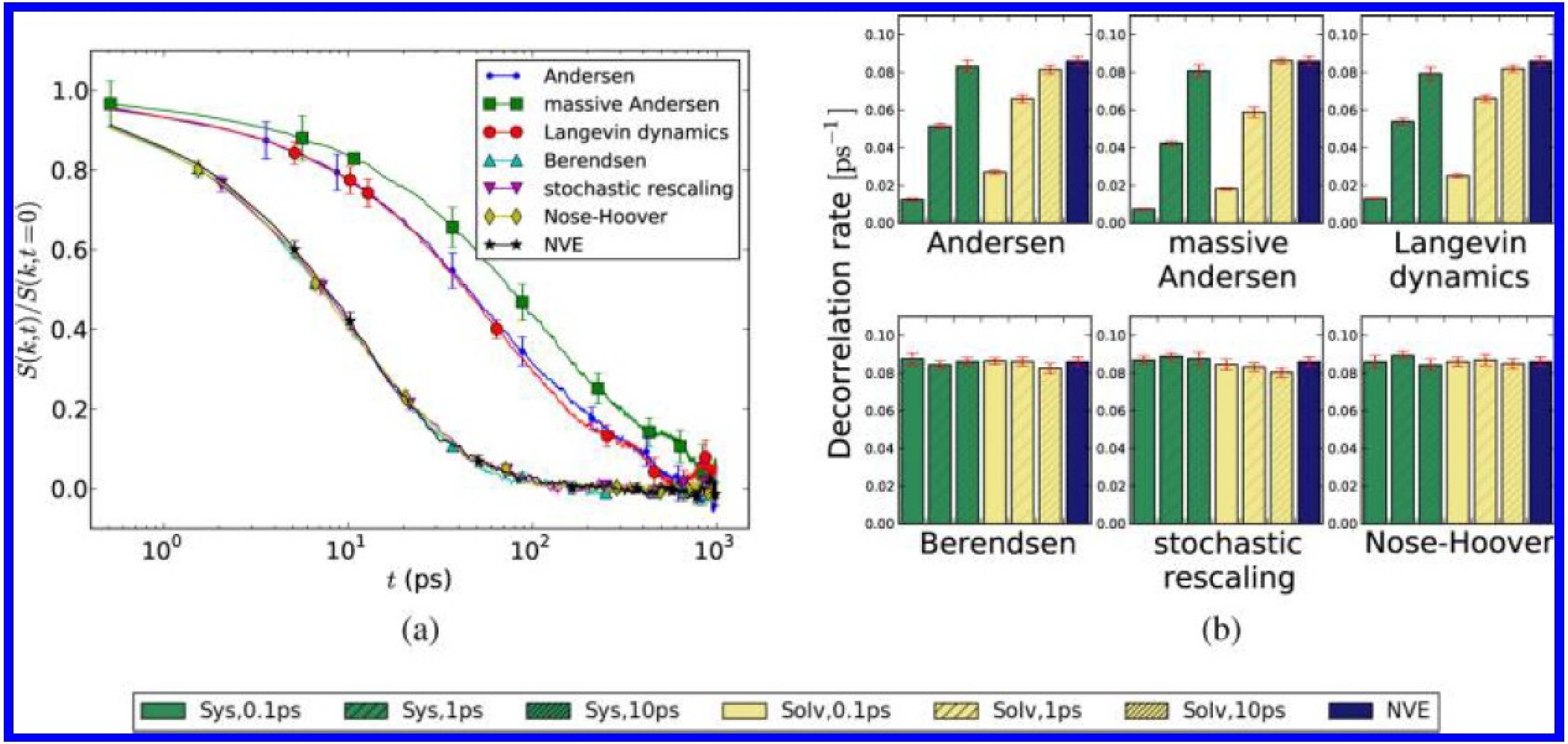
SOLUTIONS

- Use of velocity rescaling thermostats than velocity rescaling

Various thermostats with different τ_t



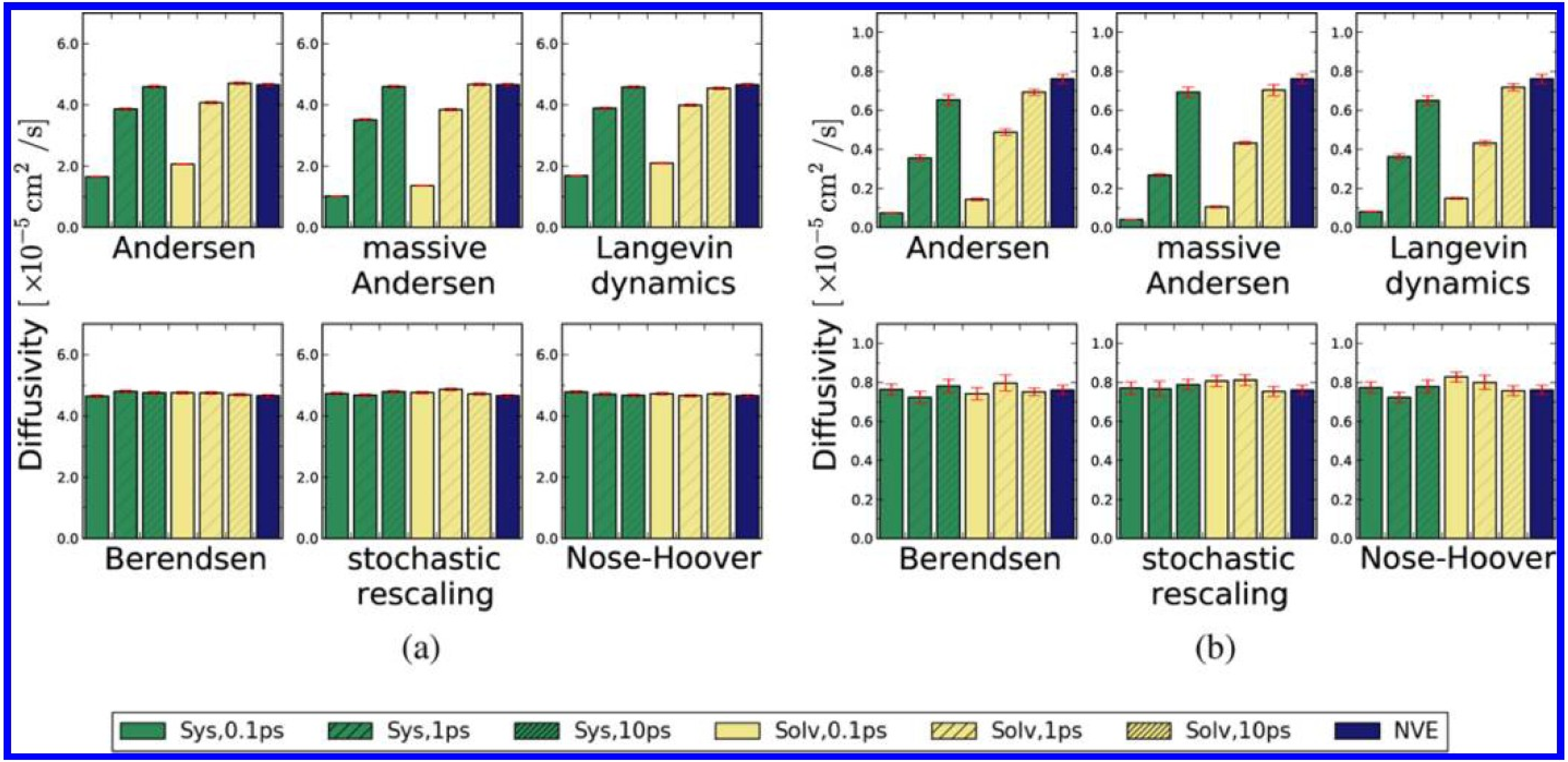
Simulations of TIP3P water model



Simulations of solvated polymer chain

SOLUTIONS

Use of Non-invasive scheme (only solvent is thermostatted and solute is connected to heat bath i.e, solvent)



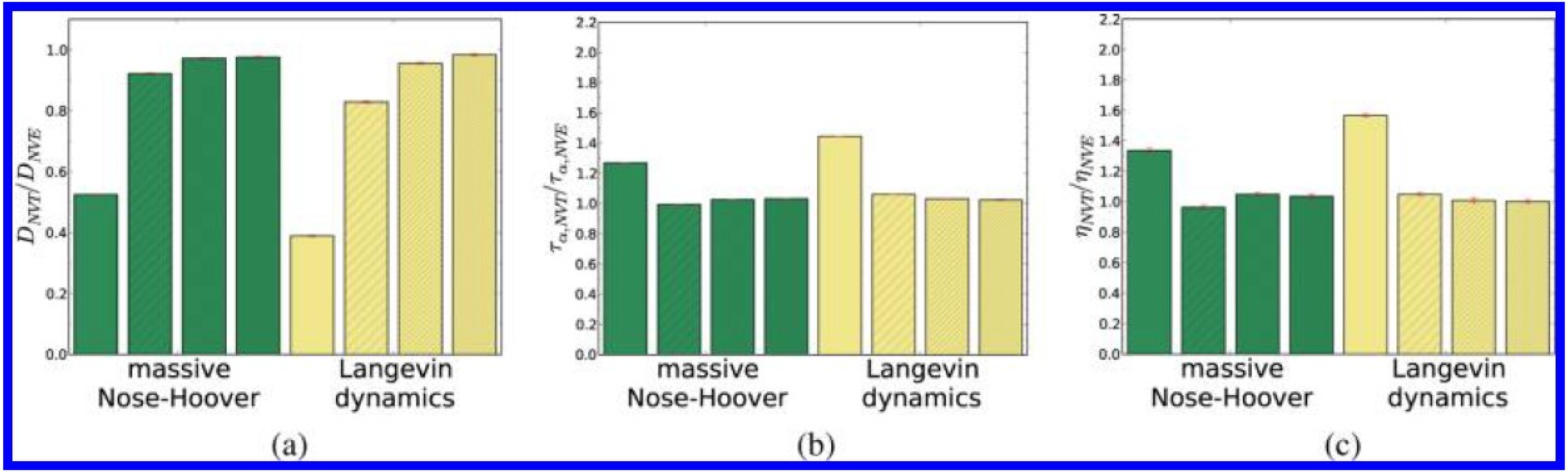
a) Simulations of solvated united-atom methane b) a solvated polymer chain

SOLUTIONS

Use of Global velocity rescaling thermostat rather than massive velocity rescaling thermostat

Global approach – the coupling constant is coupled to ensembled average Kinetic energy of the system

Massive approach- the coupling constant is coupled to individual kinetic energy of the particle



Simulations of TIP3P water with coupling constants 0.1 ps, 1 ps, 10 ps and 100 ps respectively

THANK YOU!!