Molecular Dynamics Study of Model SI Clathrate Hydrates: Effect of Guest Size and Guest-Water Interaction on Decomposition Kinetics

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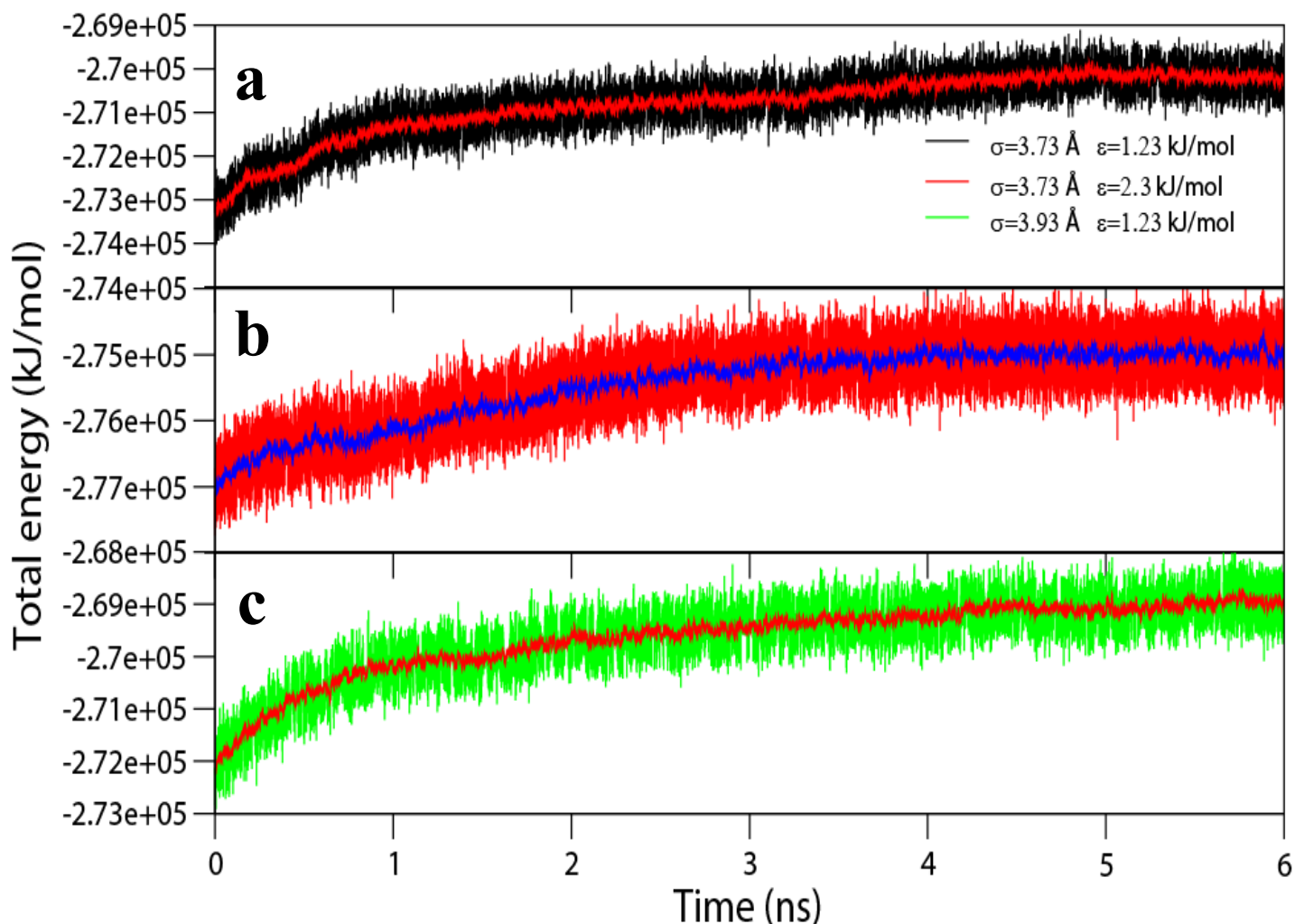Corresponding Authors: Sudip Roy and Rajnish Kumar

Figure S1: Total energy as a function of time at 310K for hydrates with different guest molecules belonging to a) σ=3.73 Å ∈=1.23 kJ/mol b) σ=3.73 Å , ∈=2.3 kJ/mol   and c) σ=3.73 Å ∈=1.23 kJ/mol

The total energy of the system is satisfactorily conserved even at higher temperatures of 310 K at 10Mpa with a maximum decrease of 0.005 % during 6 ns of simulation time.
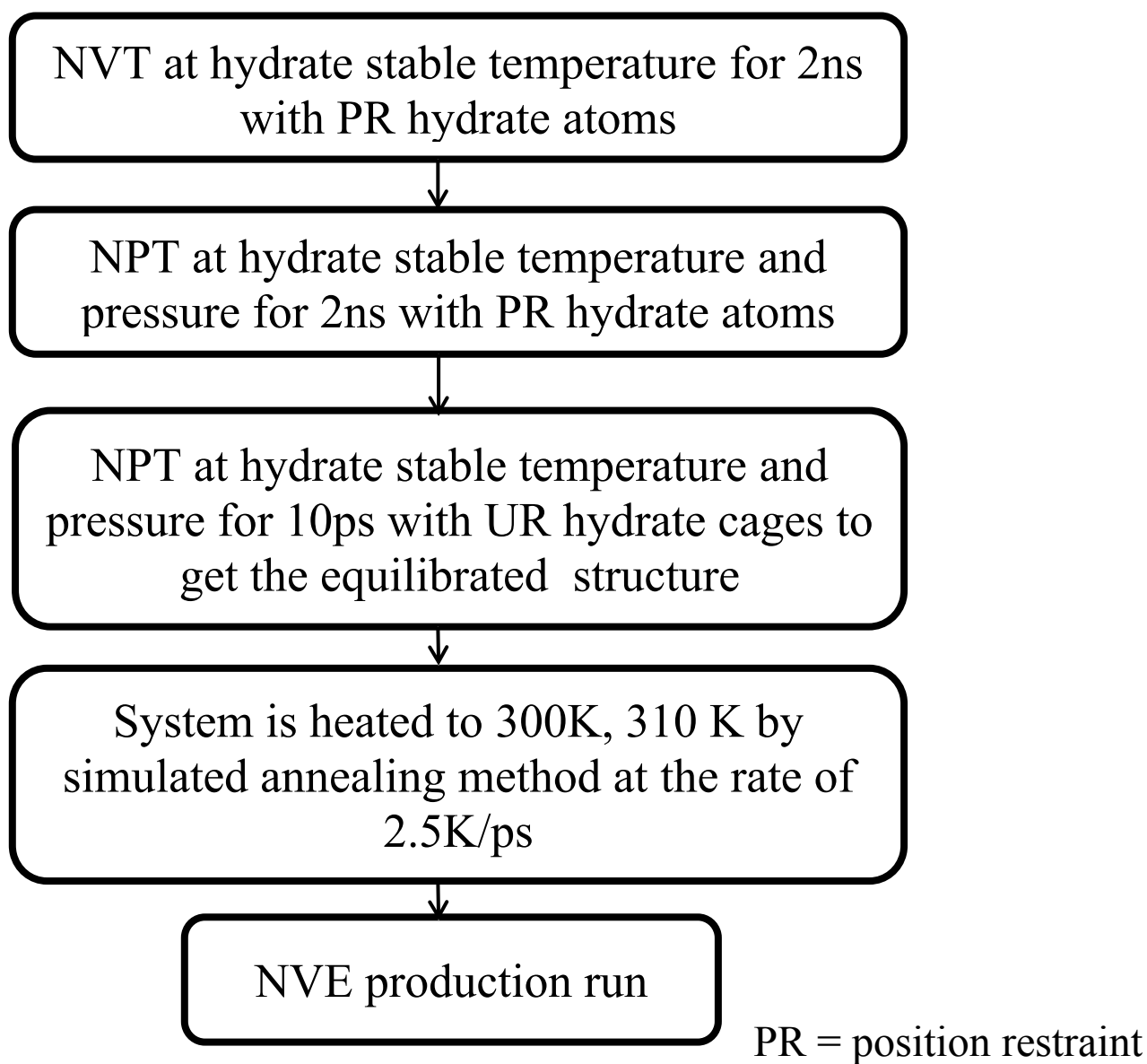
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┌─────────────────────────────────────────────┐
│   NVT at hydrate stable temperature for 2ns  │
│          with PR hydrate atoms               │
└─────────────────────────────────────────────┘
                      │
                      ▼
┌─────────────────────────────────────────────┐
│   NPT at hydrate stable temperature and      │
│   pressure for 2ns with PR hydrate atoms     │
└─────────────────────────────────────────────┘
                      │
                      ▼
┌─────────────────────────────────────────────┐
│   NPT at hydrate stable temperature and      │
│   pressure for 10ps with UR hydrate cages to │
│        get the equilibrated  structure       │
└─────────────────────────────────────────────┘
                      │
                      ▼
┌─────────────────────────────────────────────┐
│   System is heated to 300K, 310 K by         │
│   simulated annealing method at the rate of  │
│                  2.5K/ps                     │
└─────────────────────────────────────────────┘
                      │
                      ▼
       ┌──────────────────────────────┐
       │     NVE production run        │
       └──────────────────────────────┘
                                    PR = position restraint
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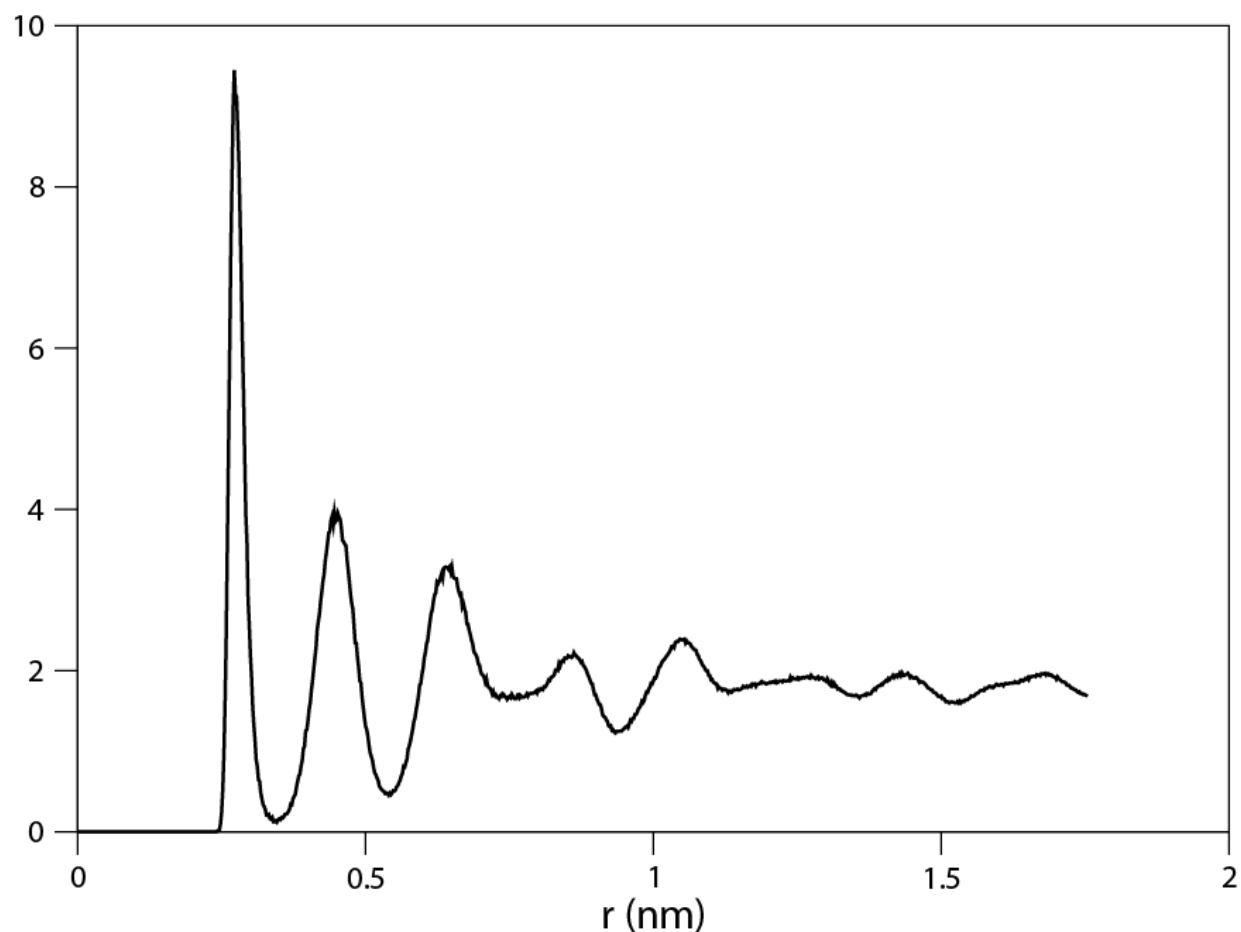
Figure S2: Simulation Flowchart

Figure S3: Radial distribution function between O-O atoms of hydrate water molecules

Figure S2 shows the radial distribution function (RDF) between O-O atoms of hydrate water molecules averaged over 10 ps for restrained NPT simulation at 273 K and 10 MPa for methane hydrate system . Here the criterion for distance was chosen as 0.3 nm for water molecules hydrogen bonded to each other for calculating torsion order parameter.
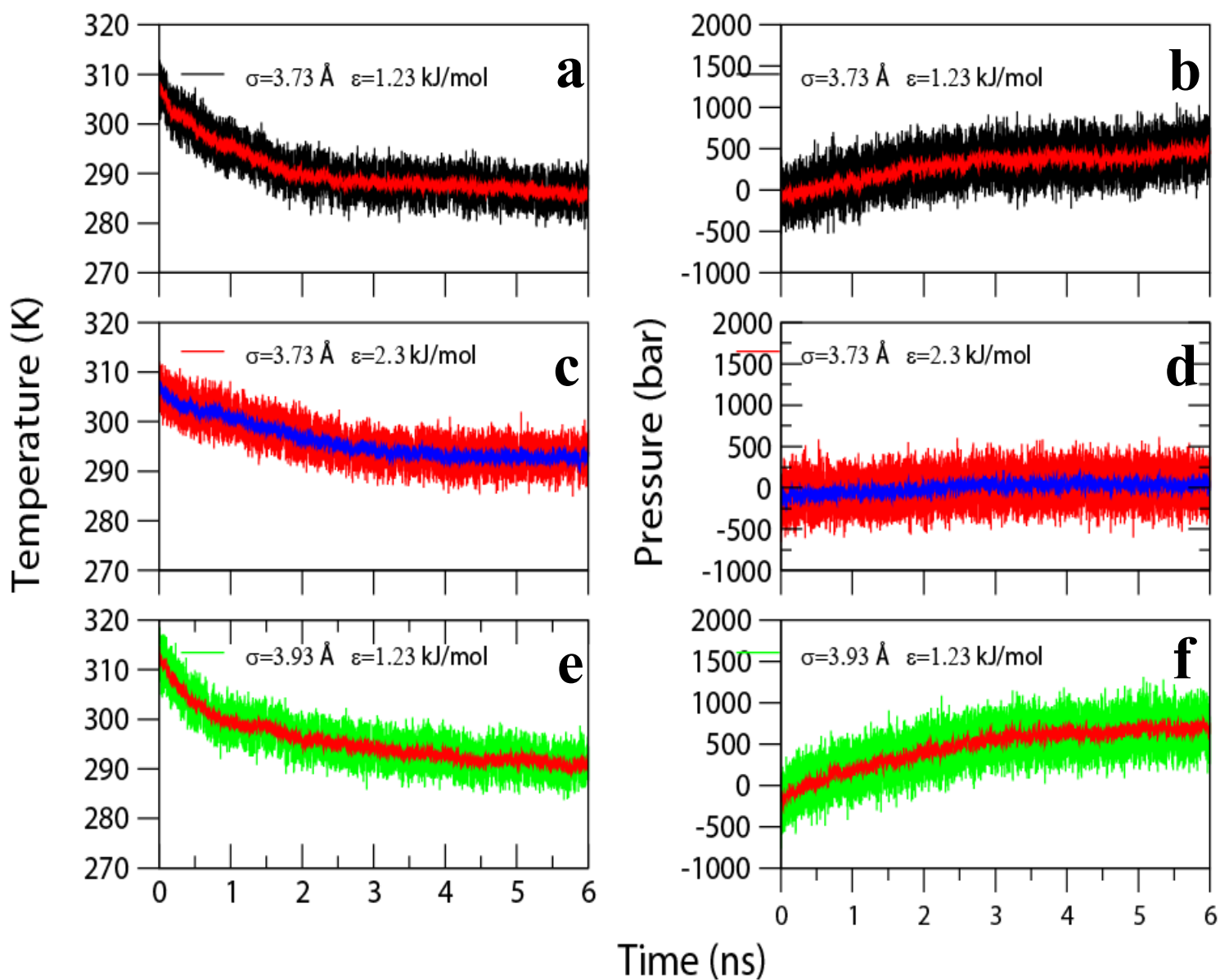
Figure S4: Temperature profile at 310K for the hydrate systems taken with different guest molecules belonging to a) σ=3.73 Å ϵ=1.23 kJ/mol c) σ=3.73 Å , ϵ=2.3 kJ/mol and e) σ=3.73 Å ϵ=1.23 kJ/mol. b),d) and f are the corresponding pressure profiles
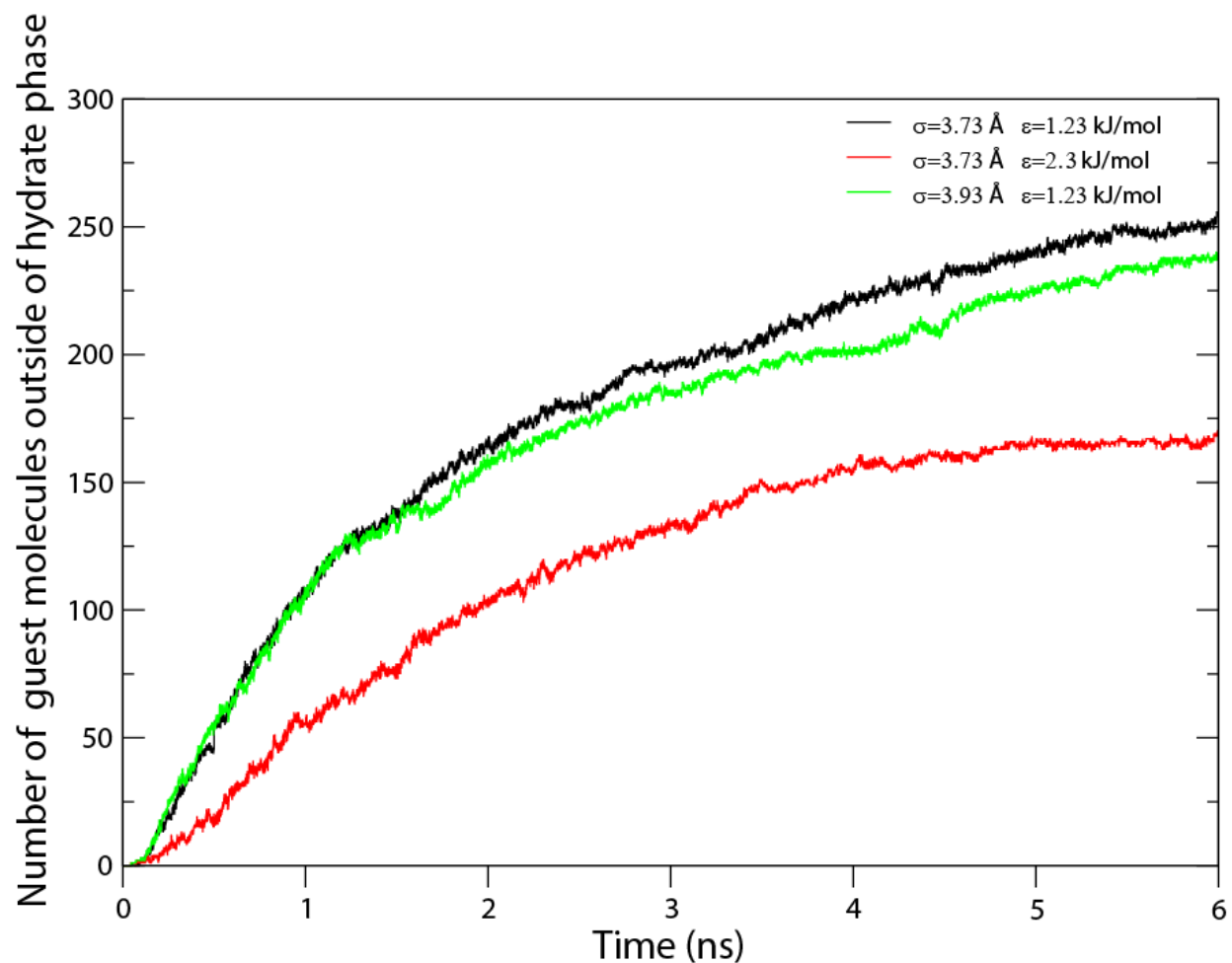
Figure S5: Plot for the number of guest molecules which has moved out of the cages as a function of time at 310K for the hydrate systems belonging to different guest molecules σ=3.73 Å ε=1.23KJ/mol ,σ=3.73 Å , ε=2.3 ,σ=3.73 Å ε=1.23KJ/mol

The plots are fitted to a straight line before the point it starts to saturate and the slope of the straight line is taken as the decomposition rate. While the hydrate system dissociates, there is a possibility of positional drift of the system. Therefore, for calculating the displacement of molecules in the whole system (hydrate phase and bulk water), the amount of drift is compensated by translating the hydrate phase at every 0.5 ps.
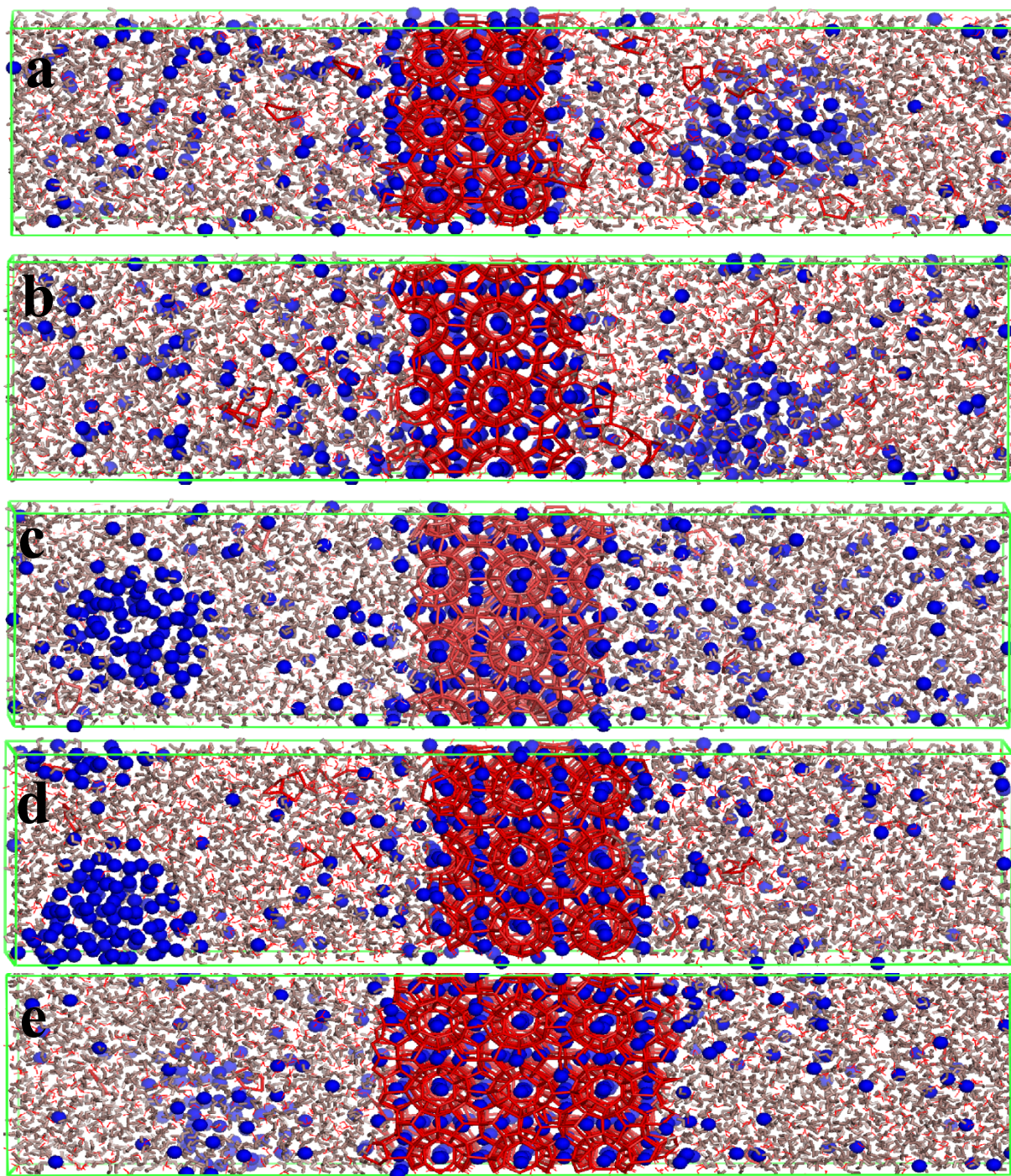
Figure S6: Figure shows the snapshot at 310K for hydrates with different guest molecules belonging to a) σ= 3.73 Å ϵ=1.03 kJ/mol b) σ= 3.73 Å ϵ=1.23 kJ/mol c) σ= 3.73 Å ϵ=1.43 kJ/mol d) σ= 3.93 Å ϵ=1.23 kJ/mol e) σ= 4.13 Å ϵ=1.03 kJ/mol
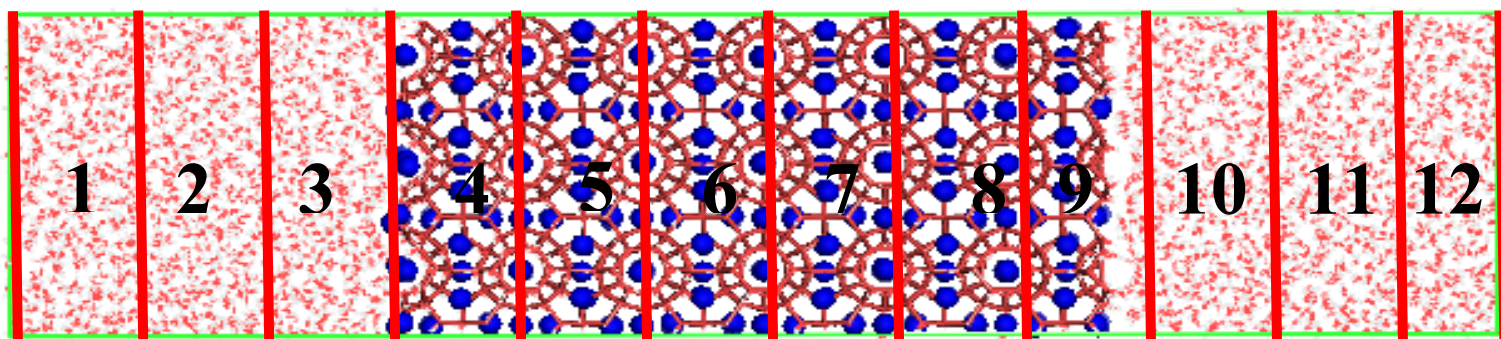
Figure S7: Division of the simulation box in twelve equal slabs along the hydrate-water interface (Z-axis)