Applications of Parallel-Tempering Methods to the Simulation of Macromolecular Systems

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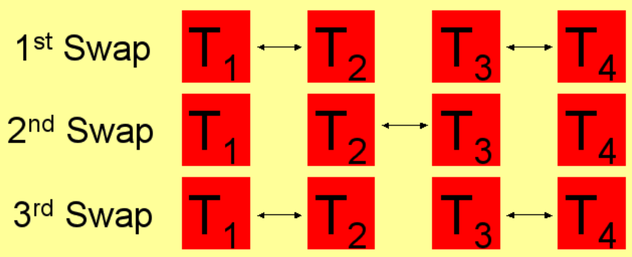
Parallel Tempering

•In a parallel tempering system a series of non-interacting replicas of a system are run at different temperatures or potentials

•At regular time intervals there is an attempt to swap two neighbouring systems while maintaining the correct Boltzmann distributions

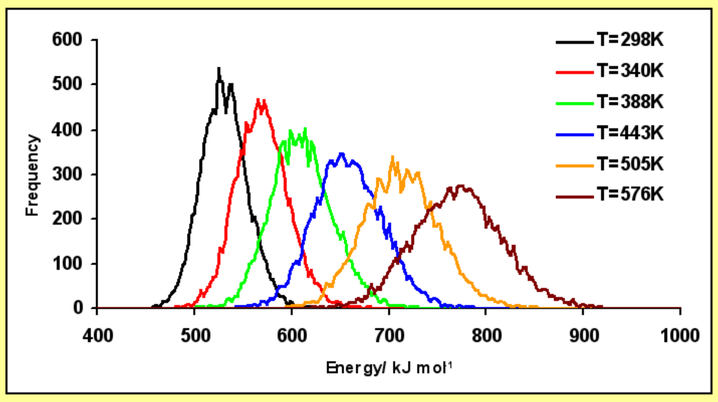


•Parallel tempering stops the system getting stuck in a molecular energy well and thus gives better sampling of the molecule

•The method was tested on a Liquid Crystal Silsesquioxane dendrimer and a united-atom alkyl chain system

•For the temperature replica case the overlap of the density of states should be equal so that swapping is equal across all nodes the temperature the different nodes should be can be calculated using

$$\frac{T_2}{T_1} = \frac{T_3}{T_2} = \ldots = \frac{T_n}{T_{n-1}}$$



Energy distributions for mesogen system at the four individual temperatures and the energy distribution of a system undergoing swapping

Potential Softening

•Rather than run a series of replicas at different temperatures you can run a series of replicas with different potentials

•By using softer potentials you can allow molecules to get much closer to one another

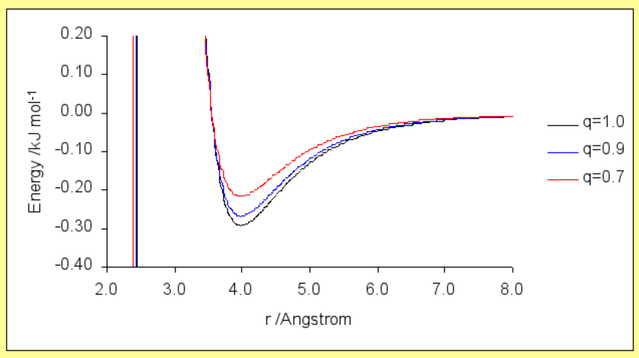
•The potential used is

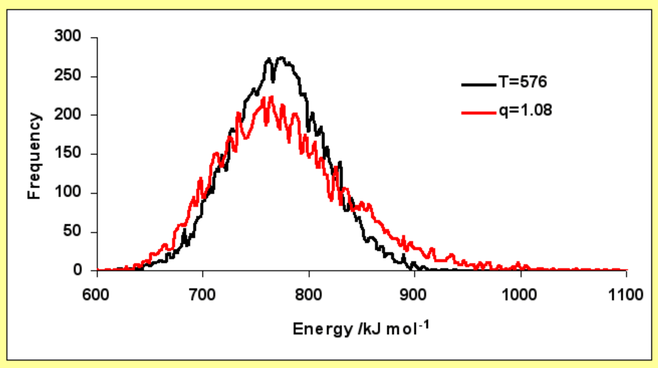
$$U_q\left(\mathrm{r}^N,\epsilon\right) = \frac{q}{\beta(q-1)}\ln\left\{1+\beta(q-1)\left[U_q\left(\mathrm{r}^N\right)+\epsilon\right]\right\}$$

where q is the scaling factor, is a energy shift parameter and the other terms have their usual meanings

•The advantage of this type of scaling is that the density of states is wider

Example of the softening on the non-bonded interactions of two carbon atoms





Example of the different shapes of the density of states plots obtained by varying temperature and potential. The density of states plot for the potential curve has a much larger tail.

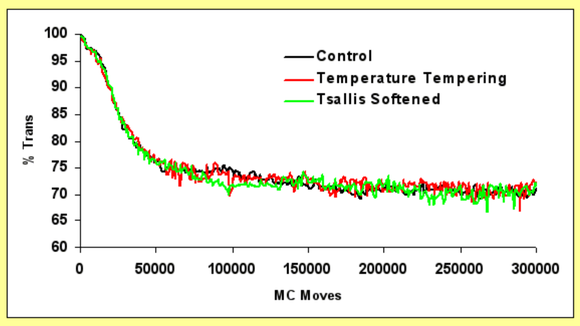
Alkyl Chain System

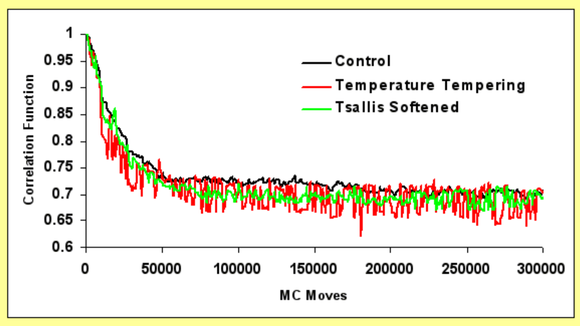
•This system consisted of 216 alkyl chains. Each chain was 11 carbon atoms long and was modelled using the united atom approach

•The chains were originally fixed in the trans conformation and the decay of the percentage of trans bonds was measured

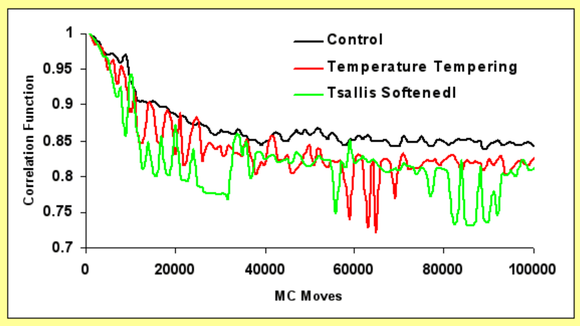
•For temperature parallel 64 replicas were set up with T_1= 298 K to T_{64}= 691 K

•In the potential softening simulation 64 replicas were set up with q_1= 1.0 to q_{64}= 3.142

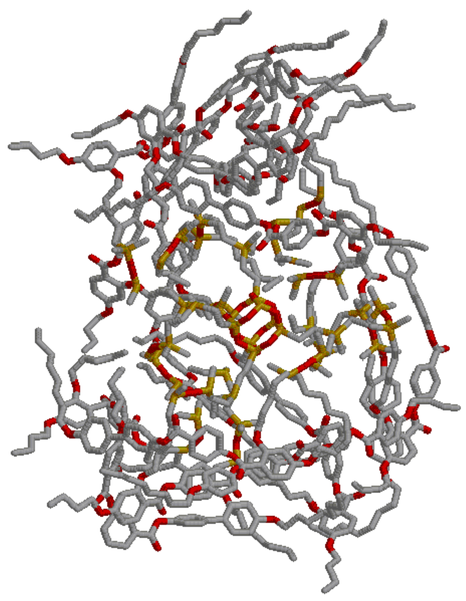




•In addition the parallel-tempering methods were also used on the equilibrated system. Here the results were much more promising (see graph of decay of correlation function to right)



Silsesquioxane Dendrimer



I.M.Saez, J.W.Goodby and R.M.Richardson, *Chem. Eur. J.*, **2001**, 7, 2758

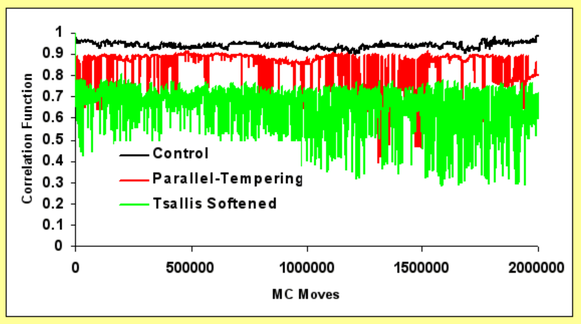
•The dendrimer has a rigid core made up of a cage of silicon's and oxygen's and 16 mesogenic arm units

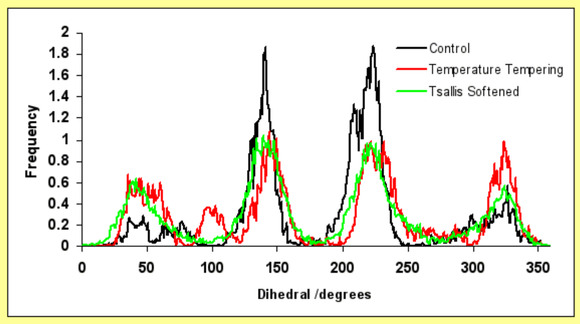
•A single dendrimer molecule in the gas phase was simulated

•For the temperature parallel-tempering 74 replicas were used with the temperature going from 298 K to 380 K

•For the potential-tempering simulation there were 32 replicas

•The effect of the parallel-tempering on the distribution of certain dihedrals within the molecule and the decay of the correlation function was looked at





Conclusions

•Parallel-tempering methods work best on systems which have poor sampling where they help the system overcome energy barriers. In systems with good sampling little difference is observed.

•Potential-softening seems to give better results than parallel-tempering. However, it is more difficult to implement as there is no standard way to assign q values prior to the simulation run.

•These methods can be combined with other methods, such as configurational bias, to allow far better sampling of molecules, which are trapped in energy wells.