A large-scale study of hyperbranched star-like polymers in high-performance computing systems.

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Overview:

The field of hyperbranched star-like polymers, developed in the late 1970s[1], has exploded during the past decade. In the very beginning they were placed only in the polymer and material science but quickly these new class of macromolecules has found its place in the interdisciplinary field between organic chemistry, medicine, biology and biotechnology.
An evaluation of their structure and behavior will detail what advantage dendrimer might have over other polymeric architecures in those fields. Just to name a few, their globular structure makes them perfect additives for lowering viscosity. Multivalency could be a useful in the case for biomedical applications. Possible cavities present in dendrimers could hinder other molecules or the active chemically terminal-groups to transport them to a target place. Those particular molecules hold huge potential addressing lots of potential applications.
Currently there is a controversy in the literature as to whether those molecules can support hollow center structure and if they do become 'colloidial-like' for high generations. This research is treating this problem by simulation means.

Enjeux scientifiques, besoin en calcul, stockage et visualisation:

The need of dealing with a realistically large system create a question of choosing a method and implementation. For our purposes of simulations of the large molecules in a melt we have decided to use Molecular Dynamic (MD) simulations that solve equation of motion for the trajectories of particles interacting through empirical pair-potential. This method been extremely succesfull to model classical many-body systems.

At each discrete time step the position and velocities of particles are written down and can be used to calculate the equilibrium and transport properties of the system. That translates into the demand of large data space. The cost of such step is usually large. Fortunatelly used algorithms seem to tranlsate well into parallel codes. A split in the memory usages into many processors made it possible to simulate bigger and more complicated molecules such as our branched polymers.

MD simulations are one of the areas where application of GPUs has grown significantly. Lack of the need of the message passing and specific graphical cards architecture speed up the calculations. On the other hand for the largest systems calculation, a spacial decomposition to spread the system among different processors and tasks is still more efficient.

We have combined those two methods.

To equilibrate the system we have mostly used HOOMD-Blue[2] (Highly Optimized Object-oriented Many-particle Dynamics -- Blue Edition) software designed to work on NVIDIA graphical cards. Their architecture was prepared for resolving complex computational problems in a little amount of time compared to a working time on CPU. This was as well a safety procedure since initial system, very unstable because of lots of overlapping molecules and loose gaussian-type bonds, could not work well with task division and communication between many processors.

For actual simulations we have used LAMMPS[3] (Large-scale Atomic/Molecular Massively Parallel Simulator) [1] code written to work on single or multiple CPUs using Open MPI. Smaller simulated systems (approx. 700,000 monomers) were treated by using 48 CPUs while the large once (up to 1,600,000) by 64 CPUs. Already equilibrated systems being stable allowed us to submit jobs with high parallelization level.

For the last stage of the workflow at HPC[4] (High Performance Computing), we needed analysis and visualisation using VMD[5] (Visual Molecular Dynamics). To avoid transferring large data or using locally a high-performance local visualization machine, we used a remote VNC server, coupled with a and remote

visualization capacities. We used an interactive VNC session on a dedicated visualization node (coupled with Virtual GL). On the user side, a simple vnc client is needed, which allowed us to use our usual workstation.

The project needs an intermediate degree of parallelization (48-128 procs communicating efficiently), but we need many of such systems to test a big parameter space (chain length, generations, in related projects also temperature or density). In this respect, the infrastructure of the mesocenter is best suited: we need more than a simple workstation available in the lab, but the high-end supercomputers using thousands of cores in one run are not useful either.

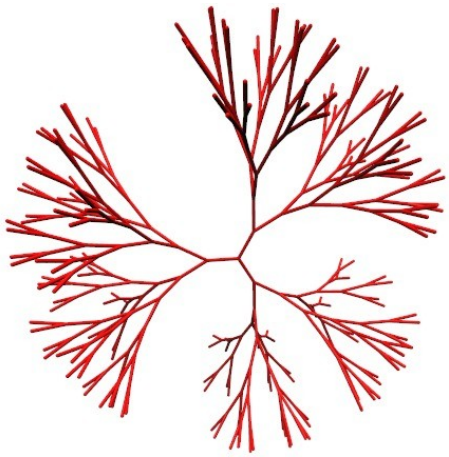
We were granted 2 access modes for the HPC center :
- a high-priority one, where we run "production-ready" jobs
- a low-priority one, where we run test and development jobs. This one was very useful to check new possiblities and test the simulation is very useful.

As well obtained 400GB is satisfying capacity for data storage for this project.

Développements, utilisation des infrastructures:

A central issue in the studies of complex structures is to understand the topological structure and then study its effects on the dynamic properties. One of the examples that we are investigating is the behavior of hyperbranched starlike polymers that is related to their architecture that is complex and need large simulation boxes. Such problems cannot be solved through experiments alone but as well through traditional software usage. Critical acceleration value in the calculation is necessary. For this reason we perform molecular dynamic simulation using two different codes, LAMMPS, that allows us to perform massively parallels simulations and HOOMD-blue, taking advantage of NVIDIA GPUs that has the potential to boost a computing capacity. Further efficient visualization and analysis is necessary and is done via remote control of a VMD session.

Complex materials despite their continuum appearance at macroscopic scales have very fine structure at microscopic scale. It is tricky to efficiently build correlations between those two scales by catching the characteristics of the micro-world and reveal the behavior of the whole sample. Timescales at what laboratory experiment are performed are not reachable by the full atomistic computer simulations. For this reason a coarse-graining method is widely used. It is capable of generating relevant insights for an efficient investigation. It closes all local details into phenomenological parameters. Once we have such general concept of a polymer, we set the topology. In our case we set large number of diverse samples where molecular mass (so the number of the beads in a molecule) and the branch lengths were changed. In the first stage equilibrium sample has to be prepared. When setting up initial configuration molecules are stretched and need to be equilibrated. A system has to be allowed to relax and reach desired equilibrium configuration. Positions and velocities were updated each timestep with the use of NVE integrator. This part was done using HOOMD-blue package. It performs molecular dynamic simulation taking advantage of GPUs to attain a level of performance equivalent to many of processor cores. Working on a simulations implemented on a single GPU, for the system containing about one million beads, HOOMD-blue performs at the same level as up to thirty processor cores worth of performance compared with a LAMMPS parallel implementation. Letting the system undergo thermal equilibration that disorders the system and drive a system into its global minimum is the first but time consuming step. Nevertheless the real problem is that it is difficult to make a clear statement saying that a sample is fully equilibrated. We have decided that stable energy, pressure, and conformation (form factor and radius of gyration) are enough to say that the real simulation runs can start. The time frame for equlibration is sample dependent (different amount of particles, chain lengths, number of branching points that made the samples relax in a different manner) and for the most complex systems it could take 10^8 reduced time steps. Final particle trajectories were obtained by using LAMMPS since a handful implementation of HOOMD-blue on few GPUs running simultaneously is still uncertain. For the biggest systems (with more then 1,5 million beads) we were using 128 CPUs. Only the smallest systems were run with 48 CPUs at ones. Each submitted job contain a run that takes one million



Simplified dendritic structure (stretched case)(VMD snapshot)

steps in reduced units, trajectory is written down on a disc and next job is submitted. Partially analysis is done on the fly. Post analysis and visualization was done using VMD. Using VirtualGL it was possible to remotely display VMD movies with full 3D hardware acceleration. Since only the rendered 3D images and not the full 3D data are send to the client machine, obtained movies were fluid. Combination of the usage of the mentioned software and methods gave us a possibility to perform fast and reliable simulation on complicated polymeric systems.

Outils, le cas échéant complémentarité des ressources, difficultés rencontrées:

Simulations, as mentionned above, were performed using LAMMPS and HOOMD-blue. Both codes were working flawlessly without unpredicted interruptions. Surely because of the high level of parallelisation LAMMPS simulations are running faster. Newertheless no problems were encountered while using the other software.

Prewiev of the system and visual analysis was possible due to the coupling of visualisation tools provided by HPC center. Visualisation with VirtualGL is easy in use and work fluently.

Further analysis of the structure was performed by self-written programs.

Résultats scientifiques:

The commonly accepted model for star-like polymers assumes a box shaped density profile called sometimes dense core model. It predicts that the density is the highest in the center and end groups being distributed throughout the volume of the dendrimer. However, to our surprise the deviations from commonly accepted density profile occurs at higher generations. Apparently generation number has an infuence on its shape.

With increasing generation the density shows a depletion close to the center. This internal inhomogenity rise a question over the compelling influences of entropy over the incompressibility. Stretched central chains means gain of entropy that result from increasing number of the accessible conformations for part of the molecule in a rising distance from the central monomer. Longer arms together with high generation number means that there will be more monomers that are able to fold back to the center. That means more crowding. The region close to the center becomes more dense and chains are not allowed to do the core interpenetration.

To conclude: interaction between monomers that did come back close to the configurational center causes steric crowding. Because of those two effects for dendrimers with high generations, only specific conformations specific conformations, with hollow center are favored.

Other interesting question during the investigatin have arised. It is needed to be checked if the systems show any evidence of entanglements or not. Molecules with long arms could penetrate neighboring ones easily. The longer the arm the less constrained are its movements since branching points are further one from another. Finding the maximum number of molecules that touch a given one would give us a hint. We call it a contact number C_n. Again we got intriguing results differing those architecture from the linear polymers. Plots of the C_n as a generation number shows a nonmonotoneus behavior. This again indicates that generations, so the number of branching points, make those structures unique.

Further performed scattering experiments ensure us that those molecules becomes more compact, and backfolding of the arms is present.

Perspectives:

In contrast to some work in the literature, our molecules show non-homogenous profile that affects its rheological behavior and could have frutiful implementations. Full picture, correlations between the static properties with the underlying dynamical behavior, will enable us to predict and explain properties of

investigated samples.

The access to the mechanical properties of the considered melt samples would demonstrate how it responds to a load, what is the stress-strain characteristics. To acheive this we have started performing shear- and oscillatory-flow experiments. Rheological material properties, like viscosity, normal stress coefficients impact at all stages of material use – from preparing to product performance. For this reason such experiment are necessery to see molecules behavior in a full picture.

Another variation of the topic is the invectigation of randomnly branched structures. These materials catch attention not only because of their unusual behavior but simply because they can be produced in a one-pot reaction. Compared to star-like regular polymers their behavior undergo wild changes when altering architecture slightely. Just the degree of branching alone have drastic effect on the behavior. Having same chemical structure but different densities, viscoelastic properties would affect the further potential applications. Structure optimalisation for a target application requires detailed research and may bring lots of intriguing results.

We are grateful to Equipex Equip@Meso for computational resources provided to us at the University of Strasbourg.

Références:

[1] Egon Buhleier, Winfried Wehner, Fritz Vögtle ""Cascade"- and "Nonskid-Chain-like" Syntheses of Molecular Cavity Topologies". *Synthesis* **1978** (2): 155–158

[2] HOOMD-blue: codeblue.umich.edu/hoomd-blue/

[3] LAMMPS: http://lammps.sandia.gov/

[4] HPC-UDS: https://hpc.unistra.fr/

[5] VMD: www.ks.uiuc.edu/Research/vmd/