Investigation of an Unusual Phase Transition
Freezing on heating of liquid solution

Calin Gabriel Floare

National Institute for R&D of Isotopic and Molecular Technologies,
Cluj-Napoca, Romania

Max von Laue
1879-1960

Paul Langevin
1879-1946

Joseph Fourier
1768-1830
Cluj-Napoca - Romania

Cluj in 1617 - Bird’s eye view by Georg Houfnagel after a painting by Egidius van der Rye.

The city center - air view from south-west (1930)
Our cluster

- **Hewlett Packard Blade C7000 with 16 Proliant BL280c G6 (2 Intel Quad-core Xeon x5570 @ 2.93 GHz, 16 Gb RAM, 500 Gb HDD) running, TORQUE, MAUI, GANGLIA ([http://hpc.itim-cj.ro](http://hpc.itim-cj.ro)), NAGIOS, configured from scratch - Scientific Linux 5.3 (Boron)**

- We installed different Intel compilers, mathematical and MPI libraries

- We are using different Quantum chemistry codes like: AMBER, GROMACS, NAMD, LAMMPS, CPMD, CP2K, Gaussian, GAMESS, MOLPRO, DFTB+, Siesta, VASP, Accelrys Materials Studio

- We are hosting also the RO-14-ITIM Grid site ([http://grid.itim-cj.ro](http://grid.itim-cj.ro))
The story of a serendipitous discovery¹

α-cyclodextrine, αCD:
the association of 6 glucose units: \((C_6O_5H_{10})_6\)

4-methylpyridine, 4MP:
\(C_6NH_7\)

…..and a bit of water

Concentration, $\alpha$CD[g]/4MP[l]

Temperature °C

Solid phase

Liquid phase

200g/l ~ 1 $\alpha$CD for 50 4MP
A movie by A. Filhol, Laue-Langevin Institute

Inverse freezing in α-cyclodextrin solutions

Azobenzene: melts at 66°C
αCD-4MP: freezes at 66°C

http://www.ill.eu/about/movies/experiments/in16-a-liquid-paradox/

ComplexHPC Spring School, May 9-13, 2011, VU University, Amsterdam, The Netherlands
Solubility $\alpha$CD in 4MP

Concentration mg/ml

Temperature °C

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How we can rationalize these surprising observations?

As temperature increases, entropy must increase, how is this compatible with the observation that crystalline order is established and that molecular motions are slowed down?

Characterize the changes of the structure and of the molecular dynamics by:

• elastic and inelastic neutron scattering
• neutron and X-ray diffraction,
• low-field NMR and
• molecular dynamics simulations
a) Hysteresis-like fixed window (elastic) scan, IN10, ILL; b) Quasi-elastic neutron spectra, IN5, ILL
**Figure 1.** Time and length scales. The left of the figure includes examples of processes that occur at different time scales. Protein association, dissociation, and aggregation (*) are concentration dependent and might span longer times than presented here. Examples of molecular size are at the top. Three simulation approaches, quantum mechanical, molecular mechanics, and molecular dynamics simulations of simplified protein models, outline the time and length scales that are accessible to these approaches. The area of the time-length scale that corresponds to molecular dynamics simulations signifies a range of simplified protein models that are used in simulations. Thus, accessing all the scales outlined might require the use of several, mutually consistent simplified protein models.

F. Ding and N. Dokholyan, Trends in Biotechnology 23(9) 450 (2005)
Model studied system:

- 2004 - NPT molecular dynamics simulations using Accelrys CERIUS$^2$ v4.6 with COMPASS forcefield running on different SGI workstation
- A periodic box with the dimensions $24\text{Å} \times 24\text{Å} \times 24\text{Å}$, containing:
  - one $\alpha$-CD molecule
  - 50 molecules of 4MP

$\rightarrow$ 826 atoms
- 20 $\alpha$-CD molecules
- 1120 molecules of 4MP
- 240 water molecules
- NPT ensemble MD using AMBER9
- $(60 \text{ Å})^3$ box

18920 atoms

- speed of 0.22ns day (1 core), 0.39ns day (2 cores) and 0.69 (4 cores)
- Infiniband is needed for a further scale up

An AMBER benchmark on IBM SP5 cluster (IBM p575 Power 5, bassi.nersc.gov, 118 8-cpu nodes, 1.9 GHz Power 5+ cpu, 2 MB L2 cache, 36 MB L3 cache, 32 GB memory per node) produced 22ns/day when using 256 cores, on a system containing around 23500 atoms.

- Initially we have to optimize the force fields using the force-matching method
- 100 ns long trajectories at different temperatures must be calculated for good statistics
- Hydrogen-bond dynamics and cluster formation analysis
- Correlation coefficients

This system will be studied at CINECA, Italy, on a project founded by HPC-Europa2 program on 256 CPUs
1 Million atoms Simulation Dream

Amber 11 GPU performance compared with that on Kracken@ORNL

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GPU Codes

ACEMD
high-throughput molecular dynamics

ZOOMED
blue

HALMD • HAL’s MD package
Highly Accelerated Large-scale Molecular Dynamics

NAMD
Scalable Molecular Dynamics

gpugromos
A GPU based solvent acceleration library for GROMOS MD++

Hardware (# GPU cores) × Performance
ACEMD 1 Fermi GPU 480 cores × 68 ns/day
ACEMD 3 Fermi GPUs 1440 cores × 110 ns/day
Reference NAMD2.7 32 cpus (128 cores)² × 64 ns/day

Model: Dihydrofolate reductase (DHFR) solvated in water, 23558 atoms, periodic boundary conditions, 9 Å cutoff with PME 64x64x64, rigid bonds, long time step scheme 4fs. ¹ System: X5570 CPUs 2.93 GHz and IB dual rail DDR.

AMBER 11 GPU Test Drive – Reduce Simulation Time from Hours to Minutes
• Milu (Miramare Interoperable Lite User Interface), a tool to set up easily an UI on (almost) any machine (https://eforge.escience-lab.org/gf/project/milu/)
• BEMuSE: Bias-Exchange Metadynamics Submission Environment (https://euindia.ictp.it/bemuse/)
• EPICO – eLab Procedure for Installation and Configuration (http://epico.escience-lab.org/)
• Training Tools: GRID Seed (http://gridseed.escience-lab.org) Moodle Platform (http://www.moodle.org)
Running AMBER on GRID

Giulio Rastelli and col. from University of Modena already deployed AMBER on GRID. Contacts were established with the institution distributing Amber regarding the license policy on the grid.

The outcome of the negotiation was that we were allowed to deploy Amber on the grid under the following conditions*:

• Each cluster deploying Amber had to have at least one license.
• Grid users allowed to use Amber had to come from one of the laboratories owning an Amber license.
• Grid users allowed to use Amber under the conditions described above could deploy their computations on all the grid clusters.

To know more about it:

**OF NOTE**

**EARTH SCIENCE**

Extraneous May stem warming in Midwest

Predicted increases in rain parts of the Midwest may reduce the temperature effect that scientists expect from global warming during the next few decades. Computer simulations of the climate in the lower 48 United States suggest that if atmospheric concentrations of planet-warming carbon dioxide rise at 1 percent per year, average temperature across the region will be at least 3°C hotter in the 2090s than it was in the 1990s, says Zaitao Pan, a climatologist at the University of Missouri, Columbia. That will boost Midwest precipitation by as much as 1 millimeter per day over the period due to a more intense circulation. The extra moisture will consume solar energy and contribute to warming. The team plans to test this hypothesis with computer models in the coming years. 

**COOL SPOT**

Temperature in portions of the Midwest might increase only by a little cold blue zone (L. Bai), a new study finds. This observation may be due to the ability of the human brain to adapt to individual circumstances, said Leonardo V. Cohen of the National Institute of Neurological Disorders and Stroke in Bethesda, Md., and his colleagues. The scientists administered a verbal test to nine adults with normal vision and nine adults who had lost their sight by age 14. Each volunteer listened to a series of spoken words, such as 500 and had 5 seconds after each one to say an appropriate verb, such as eat.

**NEUROSCIENCE**

Verbal singing in brains of the blind

Brain areas that typically play a key role in vision instead contribute to language abilities among blind people, a study finds. This observation underscores the brain's ability to adapt to individual circumstances, the study says. This ability may be due to the ability of the human brain to adapt to individual circumstances, said Leonardo V. Cohen of the National Institute of Neurological Disorders and Stroke in Bethesda, Md., and his colleagues. The scientists administered a verbal test to nine adults with normal vision and nine adults who had lost their sight by age 14. Each volunteer listened to a series of spoken words, such as 500 and had 5 seconds after each one to say an appropriate verb, such as eat.

**ASTRONOMY**

Mariner Martian water everywhere

Mariner has an ocean at least a kilometer deep and larger than the combined area of all five Great Lakes on Earth. The scientists analyzed the results of their research for signs of water and ice in the Mariner basin, Opportunity. The scientists analyzed the results of their research for signs of water and ice in the Mariner basin, Opportunity.
Law-breaking liquid defies the rules

When you place a pan of water on a stove and turn up the heat, the last thing you expect to appear is ice. However, researchers in France have discovered a liquid that “freezes” when it is heated. Marie Plazanet and colleagues at the Université Joseph Fourier and the Institut Laue-Langevin, both in Grenoble, found that a simple solution composed of two organic compounds becomes a solid when it is heated to temperatures between 45 and 75 °C. Moreover, the solidified solution becomes a liquid again when it is cooled (J. Chem. Phys. 121 5031).

Thermodynamics tells us that the entropy of a system increases when the temperature rises, which means that solids usually melt when they are heated, while liquids turn into gas. There are some exceptions to this rule. For example, heating can lead to chemical changes that cannot be reversed, such as polymerization, and quantum fluids such as helium-3 also exhibit counterintuitive phase changes. But a reversible transition in which a simple molecular liquid becomes a solid when heated has never been observed at room temperature until now.

Plazanet and colleagues prepared a liquid solution containing α-cyclodextrine (αCD), water and 4-methylpyridine (4MP). At room temperature, up to 300 g of αCD can be dissolved in a litre of 4MP, which results in a homogenous and transparent solution. When it is heated, the solution forms a milky-white solid, and the temperature at which this takes place decreases as the concentration of αCD increases.

Neutron-scattering studies reveal that the solid phase is a “sol-gel” system in which the formation of hydrogen bonds between the αCD and the 4MP leads to an ordered, rigid structure. At lower temperatures, however, the hydrogen bonds tend to break and reform within the αCD, causing the solution to become a liquid again.

The Grenoble team attributes this novel behaviour to the hydrogen bonds, and is now trying to understand the solidification mechanism in more detail. Molecular-dynamics simulations confirm that the αCD ring becomes distorted as it is heated to close to the solidification temperature. As a result, the hydrogen bonds within the αCD break up and the hydroxyl groups rotate towards the outside, allowing a network of bonds to form between the different molecules.
• PhysicsWeb, 24/09/2004
• Science News, 16/10/2004
• Physics World, 11/2004
• ILL bulletin, 11/2004
• Science et avenir, 12/2004
• Science et vie, 01/2005
• Geo magazine, german edition, 01/2005
• http://www.scienceinschool.org/repository/docs/defying.pdf
• ...
L’énigme du cristal fondant

GRENOBLE. Il durcit quand on le chauffe. Il devient liquide quand on le refroidit. Une équipe de l’ILL et de Joseph-Fourier cherchent une explication.

Un avenir dans les cosmétiques?

La chauffant entre 45 et 75° centigrades, il se pourrait que les liaisons d’hydrogène se rompent et les molécules “s’ouvrent”, ce qui leur permettrait de faire une jonction, de l’une à l’autre. D’où cette “solidification” pour le moins surprenante.

Et alors ? “Alors, expliquent Marie, Mark et Peter, nous cherchons à mieux comprendre le mécanisme de solidification, l’arrangement particulier des molécules. Ensuite, nous avancerons, progressivement.”

Pour ce faire, ils profitent bien entendu de la source à neutrons de l’ILL, mais également du rayonnement synchrotron de l’accélérateur voisin, de l’European Synchrotron Radiation Facility. Tout en s’étonnant de l’agitation du milieu scientifique provoquée par cette découverte. “Celle-ci ne date pas d’hier. Mais le temps que nous publions l’information, comme il se doit, et l’information a été rapidement réprise sur le Web, nous avons été sollicités de toutes parts.”

Alors quelles applications possibles pour ce “cristal” si changeant ? Elles pourraient se situer dans les carburants, dans la mécanique, dans la micro et la nano-électronique. Et, en y réfléchissant, cette faculté de passer aisément d’un état à l’autre pourrait même se révéler très précieuse pour les produits cosmétiques !

Olivier PENTIER
Thank you for your attention