

Multi-billion speed-up of glassy dynamics with swap Monte Carlo

Ludovic Berthier¹, Daniele Coslovich^{*1}, Andrea Ninarello^{1,2}

¹ Laboratoire Charles Coulomb, UMR 5221 CNRS, Université Montpellier, France

² Università degli Studi "La Sapienza", Rome, Italie

Introduction

- **Glasses** are amorphous solids. They do not flow, but unlike crystalline solids, they are disordered at the microscopic scale.
- They form thanks to the rapid **increase of viscosity** of liquids upon cooling below their melting temperature. In experiments it is possible to observe this dynamic slowing down over time-scales that are about **9-10 orders of magnitude** longer than the ones covered by conventional simulations.
- More efficient simulation algorithms are thus needed if we want to catch up with experiments

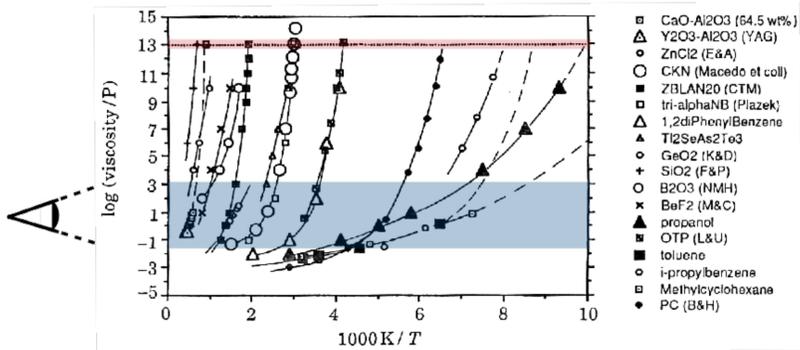
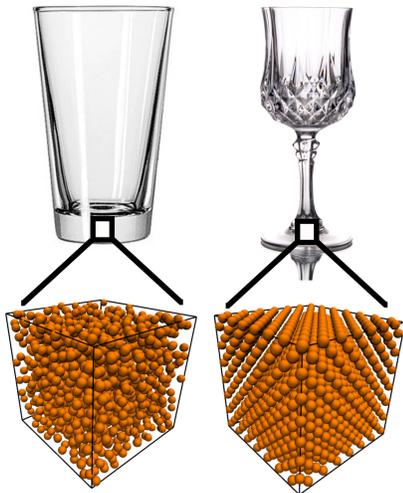


Figure 1: Viscosity of several glass-forming liquids versus the inverse temperature. The experimental equilibration limit is indicated by an horizontal red line, the viscosity range accessible in conventional simulations is indicated by the blue shaded area

Swap Monte Carlo

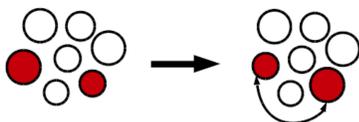
To accelerate sampling of configuration space and thus cover a broader range of time scales, we implement and optimize an efficient, swap Monte Carlo (MC) algorithm [1] in our in-house simulation codes.

At each step of the simulation, we perform the following MC moves:

With probability (1-p), we attempt to **displace a single particle** over a cube of size $dr=0.2$ (in diameter units)



With probability p, we attempt to **swap the diameters** of a random pair of particles

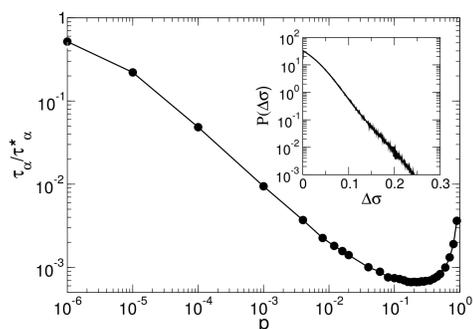


Both kinds of moves are accepted following the **Metropolis** acceptance rule, which ensures that configurations are sampled according to the equilibrium Boltzmann distribution

$$\text{Acc}_{i \rightarrow f} = \min \{1, \exp[-\frac{U_f - U_i}{k_B T}]\}$$

We adjust the parameter p to minimize the equilibration time, as measured from the decay of the time-dependent density correlation function.

Figure 2: Equilibration times as a function of the probability p of attempting a swap move. Inset shows the swap acceptance probability versus the diameter difference between the particles



Multi-billion speed-up

We simulate two classes of liquids :

- **Multi-component mixtures** (binary or ternary mixtures)
- **Polydisperse particles** (each particle has a different size)

Interaction potential

$$u_{ij}(r) = \epsilon(\sigma_{ij}/r)^n$$

Degree of polydispersity

$$\delta = \sqrt{\langle \sigma^2 \rangle - \langle \sigma \rangle^2} / \langle \sigma \rangle$$

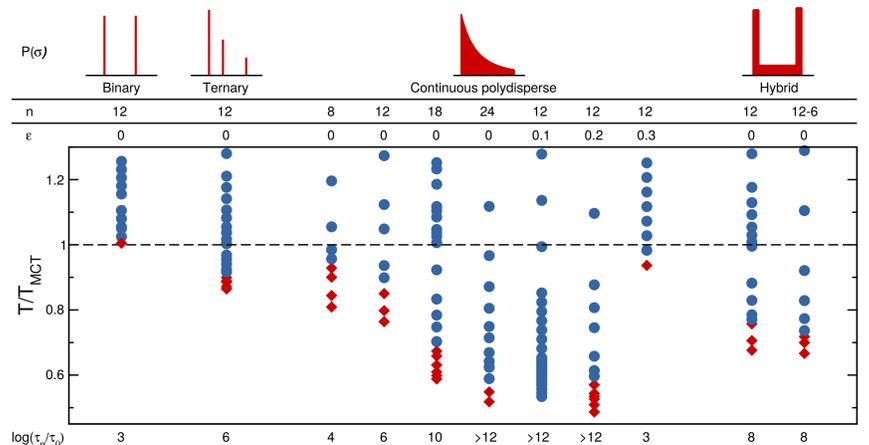
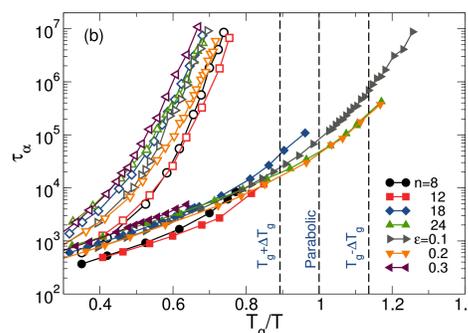


Figure 3: Temperatures at which swap Monte Carlo simulations could be performed at equilibrium (blue circles) for the studied model liquids. Red diamonds indicate temperatures at which the system displays strong tendency to crystallize.

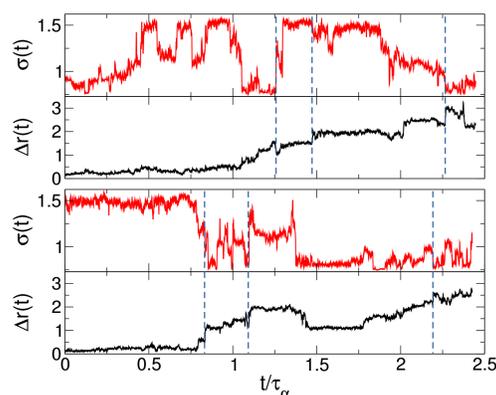


Standard MC simulations cover about 4 decades of glassy slowing down. For 23% polydisperse particles, **swap Monte Carlo** simulations equilibrate the liquid at temperatures that correspond to **13 decades of glassy slowing down!**

We perform equilibrium simulations beyond experimental limits!

Figure 4: Equilibration times of standard Monte Carlo simulations (empty symbols) and of swap Monte Carlo simulations (full symbols) for various model liquids. The vertical lines are approximate locations of the experimental glass transition.

Where is the trick?



In polydisperse systems, the diameter of the particle performs a sort of random walk in diameter space.

The **displacement** of the particle couples to the **fluctuations of the diameter**. Thus, particles can use an additional "degree of freedom" to relax from a dynamically arrested configuration.

Figure 5: Time series of the the diameter (red lines) and of the scalar displacement (black lines) of two selected particles in a polydisperse mixtures (23%). The time is scaled by the equilibration time of the system.

In this study

We have implemented and optimized a **swap Monte Carlo** algorithm to speed-up the simulation of glass-forming liquids. For systems composed of **polydisperse particles**, we achieve **speedups of more than 9 orders of magnitudes**. This enables us to study the structure of glasses under conditions that were so far not accessible, even in experiments.

References:

- [1] D. Frenkel, B. Smit, "Understanding molecular simulations" (Academic Press)
- [2] L. Berthier, D. Coslovich, A. Ninarello, M. Ozawa, Physical Review Letters 116, 238002 (2016)
- [3] A. Ninarello, L. Berthier, D. Coslovich, Physical Review X 7, 021039 (2017)