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A revolutionary methodology for modeling ultrastable polymer glasses

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Scientific context: Polymers represent a large class of materials with scores of industrial applications from tire companies to novel and more efficient batteries. Polymers can be used in a variety of thermodynamic phases which result from thermodynamical and dynamical constraints imposed by the specific molecular architecture, thermodynamic conditions, and preparation history. In particular, polymers commonly form amorphous solid states, called polymer glasses.

In fact, polymers represent just one important, but specific, example of materials that can enter glassy states of matter. Glassy states remain a poorly understood problem in the context of statistical mechanics and theoretical physics in general [1]. Computer simulations represent a central tool to study polymer glasses, as simulations grant access to detailed information about the microscopic structure and dynamics at the atomic scale. An important limitation so far has been that computer simulations operate on timescales that differ from the experimentally-relevant time regimes by a prohibitively large gap of about 8 orders of magnitude. This limitation therefore seriously limits the capabilities of computer studies to make quantitative predictions for practical applications.

Very recently, a Monte Carlo algorithm was developed to bridge the gap between computer studies and experimental work in the context of simple atomic fluids [2]. For these much simpler simple glass-forming models, a swap Monte Carlo algorithm was shown to provide an equilibration speedup by a revolutionary factor that can be at least 10^{11} for three-dimensional fluids, resulting in materials that are even more stable than experimental systems, and are therefore called 'ultrastable'. Interestingly, a novel experimental technique was recently discovered which allows the preparation of ultrastable polymer glasses also in the lab [3].

Our goal in this project is to develop a version of the swap Monte Carlo algorithm to considerably enhance the equilibration of simple models for polymer glasses. If successful, this strategy should dramatically change the performances of numerical simulations of

polymer systems, and should open novel territories to study in great detail the mechanical, structural and dynamical properties of this important class of materials.

Description of the thesis: The primary objective of the thesis is to develop novel models for polymeric systems in which it is possible to apply the swap Monte Carlo algorithm recently developed for simpler fluid systems. The first task is thus to generalise current models for polymers (for instance composed of simple monomers linked by non-linear springs) to discrete or continuous mixtures of monomers, and validate those as good computational models for polymer physics. Once size dispersity is introduced, swap Monte Carlo moves will then be introduced, and their effect on the equilibration time will be analysed. These results will guide the development of the optimal model and simulation technique to simultaneously optimise the simulated model and the algorithm. In a second part of the project, we will use the newly developed model to explore the effect of enhanced glass stability on the physical properties of polymer glasses, from dynamical relaxation at finite temperatures to mechanical properties under shear at very low temperatures.

Supervision: The thesis could take place at the Laboratoire Charles Coulomb (UMR 5221, CNRS and Université de Montpellier) and be supervised by L. Berthier (DR1, CNRS, HDR) inside the team "Statistical Physics" of the Theoretical Physics Department. The team has developed well-known expertise for the study of disordered and non-equilibrium materials, and has a large experience regarding the numerical simulations of these systems. Another possible location is the Laboratoire Interdisplinaire de Physique (UMR 5588, CNRS and Université Grenoble Alpes) and be supervised by J.-L. Barrat (Professeur) inside the team "Physique statistique et modélisation". Both groups have important numerical resources and financial support for travel and conferences. L. Berthier and J.-L. Barrat have frequently collaborated in the past on various research topics [4], have conceived the present PhD project together, and will be actively involved in the research whatever the chosen location.

Références :

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