The slow dynamics of glassy materials: Insights from computer simulations

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The physics of glasses can be studied from many viewpoints, from material scientists interested in the development of new materials to statistical physicists inventing new theoretical tools to deal with disordered systems. In these lectures I described a variety of physical phenomena observed in actual glassy materials, from disordered magnetic systems to soft gels. Despite the very large gap between experimental and numerical time windows, I showed that computer simulations represent an efficient theoretical tool which can shed light on the microscopic origins of glassy dynamics.

Glassy states of matter continue to attract the interest of a large community of scientists [1, 2, 3], ranging from material physicists interested in the mechanical properties of disordered solids, to theoretical physicists who want to describe at a more fundamental level the “glass state” [4, 5]. Glassy materials can be found in a variety of materials, from soft matter (dense emulsions, concentrated colloidal suspensions, powders) to hard condensed matter (molecular liquids, polymeric glasses, disordered magnets). Several glassy phenomena unrelated to specific materials, or even outside physics, are also discussed in this book. A feature common to glassy materials is that their dynamics gets so slow in some part of their phase diagram that they appear as amorphous frozen structures on experimental timescales. The transition from a rapidly relaxing material (liquid, paramagnet...) to a frozen structure (window glass, spin glass, soft disordered solid...) is called a “glass transition”. For many glassy materials, a full understanding of the microscopic processes responsible for the formation of glasses is still lacking.

In Fig. 1 we present snapshots obtained from computer simulations of three different models for materials characterized by slow dynamics. The left panel shows a binary assembly of Lennard-Jones particles with interaction parameters specifically designed to avoid crystallization, thus modelling either metallic or colloidal glasses [6]. The middle panel is taken from numerical simulations of a classical model for silica [7], the main component of most window glasses. The right panel shows the structure obtained in a soft gel [8] made of oil droplets in water connected by telechelic polymers (long hydrophobic chains ended by small hydrophobic heads). In the three cases, the dynamics of individual particles can get arrested on numerical timescales and the system essentially appears as a disordered solid—a “glass”. From a statistical physics point of view, two facts are quite puzzling. First, the structural properties of liquids and glasses are essentially indistinguishable. Second, there is no clear-cut phase transition between the two, so that the standard statmech language is not obviously the most relevant one to describe the formation of these solids.

Just as in many different areas in physics, computer simulations are playing an increasing role in the field of...
The answer to the first question is positive. With present day computers, it is possible to follow for instance the dynamics of \( N = 10^3 \) Lennard-Jones particles shown in Fig. 1 over 9 decades of time using about 3 months of CPU time on a standard PC, thus covering a temperature window over which average relaxation timescales increase by more than 5 decades, quite a dramatic slowing down. However, at the lowest temperatures studied, relaxation is still orders of magnitude faster than in experiments performed close to the glass transition temperature. Nevertheless, it is now possible to numerically access temperatures which are low enough that many features associated to the glass transition physics can be observed: strong decoupling phenomena \([11]\), clear deviations from fits to the mode-coupling theory \([6]\) (which are experimentally known to hold only at high temperatures), and crossovers towards activated dynamics \([12]\). Of course, smaller timescales are accessed when simulating more complex systems, e.g. silica where Si and O atoms also carry charges and interact via a long-range Coulomb interaction, or more complex situations, e.g. boundary driven shear flows \([13]\), aging phenomena \([14]\), or gel formation \([15]\).

The answer to the second question (what do we measure?) occupies the rest of this text. First one must make sure that the glassy dynamics one seeks to study is at least qualitatively reproduced by the chosen numerical models, which are necessarily simplified representations of the experimental complexity. One can for instance devise "theoretical models", such as the Lennard-Jones liquid shown in Fig. 1, which indeed captures the physics of glass-forming liquids \([6]\). One can also devise models inspired by real materials, such as the BKS model for silica and the connected microemulsion shown in Fig. 1. The major signatures of glassy dynamics are indeed easily reproduced in simplified models and can therefore extensively be studied in computer simulations: slow structural relaxation, sudden growth of the viscosity upon lowering the temperature, aging phenomena after a sudden quench to the glass phase, non-Debye (stretched) form of the decay of correlation functions. Kob has given an extensive account of these phenomena in the proceedings of a previous school \([16]\).

The important topic of dynamic heterogeneity, which emerged as an important aspect of glassy materials during the 90s, is not covered in Kob’s lectures, but alternative reviews exist \([17]\). Although different phenomena usually go under the same name, dynamic heterogeneity is generally associated to the existence, and increasing strength as dynamics gets slower, of non-trivial spatio-temporal fluctuations of the local dynamical behaviour.

Perhaps the simplest question in this context is as follows. On a given time window, \( t \), particles in a liquid make the average displacement \( \bar{d}(t) \), but the displacement of individual particles is distributed, \( P(d, t) \). It is well established that \( P(d, t) \) acquires non-Gaussian tails which carry more weight when dynamics is slower. This implies that relaxation in a viscous liquid must differ from that of a normal liquid where diffusion is Gaussian, and that non-trivial particle displacements exist. A long series of questions immediately follows this seemingly simple observation. Answering them has been the main occupation of many workers in this field over the last decade. What are the particles in the tails effectively doing? Why are they faster than the rest? Are they located randomly in space or do they cluster? What is the geometry, time and temperature evolution of the clusters? Are these spatial fluctuations correlated to geometric or thermodynamic properties of the liquids? Do similar correlations occur in all glassy materials? Can one predict these fluctuations theoretically? Can one understand glassy phenomenology using fluctuation-based arguments? Can these fluctuations be detected experimentally?

Although the field was initially principally driven by elegant experiments detecting indirect evidences of the existence of dynamic heterogeneity, and by a series of numerical observations in model liquids or simplified glass models, theoretical progress has been somewhat slower. It took some more time to realize that dynamic heterogeneity could be studied using a set of well-defined correlation functions that can be studied either theoretically, in computer experiments, or in real materials, thus allowing (in principle) a detailed comparison between theory and experiments \([10,20]\).

The main difficulty is that these correlates, unlike, say, traditional scattering functions, usually involve more than two points in space and time and represent therefore quite a challenge for computer simulations, but even more in experiments. To detect spatial correlations of the dynamics one can for instance define “four-point” spatial correlates, involving the position of two particles at two different times, a quantity which can be directly accessed in simulations. Several such measurements have been performed, and directly establish that the dynamical slowing down encountered in glassy materials is accompanied by the existence of a growing correlation lengthscale over which local dynamics is spatially correlated \([16,20]\). Together with theoretical developments \([21,22,23]\), these results suggest that the physics of glasses is directly related to the growth of dynamic fluctuations, similar to the ones encountered in traditional phase transitions \([27]\).

Experimentally detecting similar multi-point quantities in, say, a molecular liquid close the glass transition would require having spatial resolution at the molecular level over timescales of the order of the second—a real challenge.
Techniques have been devised to access these quantities in colloidal systems where microscopic timescales and length-scales are more easily accessible. Additionally, recent work has suggested that alternative multi-point correlation functions could be more easily studied in experiments, while containing similar physical informations.

Despite being performed at lower temperatures and for liquids that are much more viscous than in simulations, dynamic lengthscales measured in experiments are not much larger than in simulations. Typically, one finds that relaxation is correlated over a volume containing (at most) a few hundreds of particles at low temperature. This means that even on experimental timescales, where dynamics is orders of magnitude larger than in numerical work, there is no trace of “diverging” lengthscales, as would be necessary for simple scaling theories to apply. Such modest lengthscales are, however, physically expected on general grounds: Because dynamics in glassy materials is typically thermally activated, a tiny change in activation energy (possibly related to an even smaller growth of a correlation lengthscale) translates into an enormous change in relaxation timescales.

Although very few experimental results have been published, it seems that the dynamics of very many molecular liquids, and perhaps also of different types of glassy materials, could be analyzed along the lines of Ref. [25], perhaps leading to a more complete description of the time and temperature dependences of spatial correlations in a variety of materials approaching the glass transition. It remains to be seen if these correlations can successfully and consistently be explained theoretically, with precise predictions that can be directly confront to experimental results with decisive results.

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[27] Spin glasses are one example where this behaviour is obviously realized since three-dimensional spin glasses undergo a genuine phase transition towards a spin glass phase characterized by the divergence of a correlation length measured via four-spin correlations, a static analog of the four-point dynamic functions mentioned above. During the school, however, it appeared that students did not seem to consider spin glasses as the most exciting example of “complex systems”.