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Metastable Glassy States Under External Perturbations

Monitoring the Effects of Compression and Shear-Strain

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Corrado Rainone

Metastable Glassy States Under External Perturbations

Monitoring the Effects of Compression and Shear-Strain

Doctoral Thesis accepted by
Sapienza University of Rome, Italy

Springer

Author
Dr. Corrado Rainone
Department of Chemical Physics
The Weizmann Institute of Science
Rehovot
Israel

Supervisors
Prof. Giorgio Parisi
Department of Physics
Sapienza University of Rome
Rome
Italy

Dr. Francesco Zamponi
Laboratoire de Physique Théorique
École Normale Supérieure
Paris
France

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Alla mia famiglia,
e ai miei amici a Roma, a Parigi,
e ovunque altro li porterà la vita.

Supervisor's Foreword

Since its first conceptualization at the hands of Boltzmann at the end of the 19th century, statistical mechanics can be, as of today, considered a rather mature branch of theoretical physics. Its most well-known and remarkable success story is without much doubt the theoretical framework that it provides for the description of second-order phase transitions, whose foremost and most pedagogical examples are the ferromagnetic transition in magnetic systems and the liquid-gas transition in particle systems.

Thanks to statistical mechanics, we are today equipped with a set of theoretical pictures and tools which provide a full understanding of the phenomena which underlie the physics of those systems, on both quantitative and qualitative level. We now know that all these critical phenomena can be understood in terms of a competition between order-inducing potential energy and disorder-inducing entropy; we are able to compute, say, the critical exponent which characterizes the critical behavior of the specific heat of a ferromagnet approaching the Curie point down to three digits of accuracy, getting a result in agreement with even the most accurate experiments; and thanks to the remarkable property of universality, with its theoretical justification provided by the theory of critical phenomena, we know that the results so obtained will be valid for all the systems which happen to share the same universality class.

The tools and concepts, which have enabled us scientists to obtain this cornucopia of results, from mean-field theory, to the concept of spontaneous symmetry breaking, to the renormalization group, have been proven useful in (and in some cases, fundamental to) other branches of physics, such as the Standard Model of fundamental interactions, and today constitute the bulk of any graduate school-level curriculum in theoretical physics.

In summary, statistical mechanics has today reached paradigmatic status. Yet, despite this success, there is still a large class of systems and phenomena whose description in terms of a statistical mechanical treatment is not only lacking today, but doesn't even look forthcoming in the future: we are talking, using perhaps a too much vague terminology, about disordered systems.

A paradigmatic example of such a system is a disordered ferromagnet, wherein the interaction between magnetic dipoles fluctuates randomly in space instead of being a constant, as it is the case for an ordinary ferromagnet; another example is provided by structural glasses, wherein particles are frozen in a solid-like manner around an amorphous structure which lacks the long-range order of a crystalline solid. Despite these last two cases being the most well-known, more examples could be mentioned, including disordered quantum systems.

The presence of disorder throws off almost all of the conceptual pillars which we are used to rely on. The presence of disorder makes it impossible to discern a clear pattern of symmetry breaking; the disordered nature of the coupling constants means that implementing usual renormalization group techniques is but a futile endeavor; the lack of long-range order makes ordinary correlation functions a completely useless tool when it comes to studying critical properties and, perhaps most importantly, all those disordered systems share the cardinal feature of reaching an equilibrium state very slowly, on timescales which are comparable or larger than the typical experimental times, while the most basic assumptions at the heart of statistical mechanics rely on equilibration and ergodicity as the two main justifications for introducing a description of an evolving system in terms of a statistical ensemble.

In summary, these systems pose challenges which go much beyond mere (however undoubtedly difficult) technical issues, but concern the very nature and fundamental concepts and assumptions of statistical mechanics, and sit at the cutting-edge of the research effort in the field.

As I said above, a full framework for the description of disordered systems and their phase transitions is not a reality as of today. However, success stories and viable proposals do exist. One of these is the theory of mean-field spin glasses (i.e. ferromagnets with strong disorder) based on the method of replicas and the concept of replica symmetry breaking.

The main merit of this framework lies in the fact that it is able to bring back the basic concepts of spontaneous symmetry breaking, order parameters, and correlation functions, in a setting wherein they had apparently been made unviable or useless by the presence of disorder; this makes it again possible, for example, to write a field theory à la Landau which is in principle amenable to a renormalization group kind of approach.

Another merit is how it has shown a degree of universality which seems to be comparable to the one attained by the theory of ordinary critical phenomena: a conjecture formulated in the late eighties by Kirkpatrick, Thirumalai and Wolynes asserts that the methods and concepts of Replica Theory employed in the treatment of spin glasses are also relevant for the physics of structural glasses, somewhat echoing the shared universality of the ferromagnetic and liquid-gas transitions; this set of conjectures and ideas later coalesced in what is today referred to as the Random First Order Theory (RFOT) of the glass transition.

As of today, we know for a fact that at mean-field level the conjecture is correct. However, the accomplishment of proving its worth out of that setting has not yet

been achieved and today constitutes one of the most extensive and prolific endeavors in this field of research.

Dr. Rainone's thesis is part of this endeavor. In particular, it deals with one of the basic problems enunciated above, namely the one of slow relaxation and consequent metastability of structural glasses when looked at on typical experimental timescales.

As said above, this intrinsically jeopardizes the very possibility of a statistical mechanical description; the thesis shows how this difficulty can be worked around using the theory or replicas and how it can be applied, if only at mean-field level, to a realistic and canonical model of glass former, enabling us to reproduce known observations about metastable glasses and to formulate new predictions about their nature. The theory derived is fully analytic, going all the way from the mathematical model to tangible physical observables such as equations of state and stress–strain curves, from the microscopic to the macroscopic, in a true statistical mechanical fashion, applied here for the first time to amorphous systems out of equilibrium.

The predictions summarized in this thesis are already contributing to setting the course for future research in the field, and some of them have been already verified in numerical settings. The thesis is written in a pedagogical manner, wherein all the conceptual links and passages are thoroughly justified and explained, and calculations are reported step by step; it contains an extensive introduction to fundamentals the glass problem and the theories put forward so far to explain it, not only RFOT. It will, therefore, be a useful read for students willing to approach the problem for the first time, and who will therefore be in need of understanding both the numerous phenomenological facets of the glass problem and the physics of disordered systems, and the (sometimes obscure) mathematical and conceptual subtleties of the replica method.

This thesis is, therefore, a piece of work which combines the performance and report of cutting-edge research with a textbook-like level of pedagogy, which I believe will make it interesting to a vast public including both veteran researchers and new students willing to enter the field.

June 2017

Prof. Giorgio Parisi
Dipartimento di Fisica,
Sapienza Università di Roma,
Roma, Italy

Abstract

This thesis sums up the research work I performed as a Ph.D. student in Sapienza Università di Roma, and École Normale Supérieure, Paris, under the joint supervision of Prof. Giorgio Parisi and Dr. Francesco Zamponi. The thesis focuses on the theoretical study of metastable glasses prepared through non-equilibrium protocols.

The book is organized as follows: in Chap. 1, we give a general introduction on the problem and delineate our aims, along with an exposition of the fundamental phenomenological features of the glass problem (with emphasis on the central phenomenon of the glassy slowdown) whose reproduction is a minimal requirement for any theory of the glass transition. In Chap. 2, we give the fundamentals of one such theory, the Random First Order Theory (RFOT) which constitutes the central conceptual pillar of the present work, with emphasis on the concept of metastable state which will be pivotal in the following; in Chap. 3, we review the phenomenology of glasses as measured in experiments and simulations, in particular differential scanning calorimetry and quasi-static shear strain deformation, corresponding to adiabatic changes of the temperature T and of the strain parameter γ, respectively; in Chap. 4 we present and review in detail the state following construction, along with some of the other tools which can be used within RFOT to approach the problem of metastability in general; in Chap. 5 we perform the state following computation for the HS model in the mean-field limit, assuming the simplest possible structure for a glassy minimum (i.e. a simple paraboloid), and present the results so obtained; in Chap. 6 we dispense with this last assumption and perform a more general computation for a arbitrarily complicated structure of the glassy minima, and present the results so obtained; in Chap. 7 we provide some comparison with numerics in a simple, modified HS model which allows for a simple analytical treatment and is also very easy to simulate; finally, in Chap. 8, we summarize our conclusions and provide some suggestion for further research in the field of glass physics.

The results presented in this thesis have been already published in journal articles, but here we present them in a coherent and self-contained manner. We refer the interested reader to:

- Chapter 5: C. Rainone, P. Urbani, H. Yoshino, F. Zamponi, "Following the Evolution of Hard Sphere Glasses in Infinite Dimensions under External Perturbations: Compression and Shear Strain", *Phys. Rev. Lett.* **2015**, *114*, 015701, DOI 10.1103/PhysRevLett.114.015701.
- Chapter 6: C. Rainone, P. Urbani, "Following the evolution of glassy states under external perturbations: the full replica symmetry breaking solution", *Journal of Statistical Mechanics: Theory and Experiment* **2016**, *2016*, 053302.
- Chapter 7: M. S. Mariani, G. Parisi, C. Rainone, "Calorimetric glass transition in a mean-field theory approach", *Proceedings of the National Academy of Sciences* **2015**, *112*, 2361–2366, DOI 10.1073/pnas.1500125112; and P. Charbonneau et al., "Numerical detection of the Gardner transition in a mean-field glass former", *Phys. Rev. E* **2015**, *92*, 012316, DOI 10.1103/PhysRevE.92.012316.

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Chapter 1
Introduction

1.1 Equilibrium Supercooled Liquid Versus Metastable Glasses

This thesis is about glass. As stupid as this assertion looks, it is indeed important to state this fact loud and clear, at the very beginning.

Why is such an assertion necessary or even appropriate? The glass transition is one of the great unresolved problems in condensed matter physics (as the introduction of pretty much every work on the subject loves to remind) and it has been so for decades. And for decades, research has been produced, and still is, to investigate its nature. A thesis in the field of the physics of the glass transition which says about itself "this thesis is about glass" is therefore stating an obvious tautology, at the very best. The aim of this introduction is to have the reader understand that it is not so, and that indeed the theoretical research on the properties of glasses (as opposed to the huge amount of experimental and numerical work that has been done, and is still being done) is a relatively new subject that we are beginning to explore now.

But a pressing question then arises: what were those "decades of research" referred to above, about? The answer is: not glasses. Or rather, there has been, yes, a ponderous amount of *experimental* research about glasses over the last decades (Tool's works about fictive temperature are an example), which we will reap and use in this thesis. But the *theoretical* research, the research aiming to describe glass-related phenomena at first principle level, has not been very concerned with glass itself. Rather, most of the theoretical efforts carried out up to now are about supercooled liquids, that is, about *equilibrium* properties of glass formers.

This distinction is very important, and yet oftentimes forgotten. Despite this, it is indeed pretty obvious from an intuitive point of view. Every research article about the glass transition will at some point or another contain a sentence of the sort "...it is impossible to obtain data in this regime due to the extremely large time needed to equilibrate the sample...", and indeed, the reason why the glass problem is still open lies mainly in the fact that data in the deeply supercooled regime are, to state it in an unambiguous way, impossible to obtain. And yet, in everyday life, glasses are just

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everywhere and are indeed quite easy to manufacture; they are not a rare and exotic commodity. But despite this, the impression that one gets from the literature is that getting new data to better understand the glass problem is always sort of a struggle.

The distinction above makes it clear why: what researchers have been, and still are, mostly concerned about is the supercooled liquid. And supercooled liquids, unlike glasses, are indeed very rare and very valuable objects. It is indeed a fact that the various theories about the glass transition that are on the table today (Random First Order, Dynamic Facilitation, Frustration Limited Domains etc.) were conceived first and foremost as theories about supercooled liquids rather than glasses, and their most defining predictions concern the supercooled regime; this is the reason why it is into that hard-to-reach regime that those much needed data are to be searched for. In such a scenario, the glass is at best seen as an enemy (interestingly, much like the crystal) who sneaks in during your simulation/experiment and ruins your day by pushing out of equilibrium your precious supercooled liquid sample.

In this thesis, we are concerned with glasses.

The problem with formulating a theory about glass lies in the fact that a glass is an intrinsically *out of equilibrium* object, as opposed to the supercooled liquid. This simple fact is at the origin of all problems that are commonly encountered when trying to conceive a theory of glasses. If the theorist is aiming for a first-principle theory, then the obvious starting point is of course statistical mechanics, as in all other branches of theoretical condensed matter physics. But statistical mechanics is a framework mainly concerned with the properties of *equilibrium* systems, whose thermodynamic state is stable, and whose lifetime is infinite. Glass has no such property, as we enunciated before: its properties depend of the time t and a glass does not live forever, but only until the glass former is able to relax and flow again like a liquid. There are theoretical tools conceived for the treatment of out-of-equilibrium scenarios, but they are all meant to deal with situations wherein the system is subject to a drive of some sort (say, an AC current), and they are meant for systems with long-range order. Glass is amorphous, and is out of equilibrium because it did not have enough time to relax, not because we are perturbing it in some way. So those tools are not suitable for our problem.

At this point, it looks like a meaningful theory of glass cannot make do without a time-based description, a view which the Dynamical Facilitation Theory (DFT), for example, embraces heartily; however, the dynamics of generic many-body systems, and in particular glass formers, does not enjoy a unified and commonly accepted first-principles framework such as the one that statistical mechanics is able to provide for systems in thermodynamic equilibrium. We will see over the course of this thesis that this weakness is manifest within DFT, whose models are necessarily phenomenological in nature and never start from a microscopic, first-principles description of the glass-forming liquid. So, it looks like one is between the proverbial rock and hard place: to have a first-principles theory, one must try to rely on dynamics; but to rely on dynamics, the theoretician necessarily has to sacrifice something in terms of microscopic description (like in DFT) or simplifying assumptions (like in Mode Coupling Theory).

However, if one actually looks at how the properties of a glass change over time (for example, its internal energy U as a function of time, or any other convenient observable), one can see that the dependence on t is actually pretty simple, i.e. the dynamics looks like a *quasi-equilibrium* process wherein the observables of the system remain stable over very long time periods, of the order of the impossibly long equilibration time needed to observe the supercooled liquid. This picture of glass as a system in quasi-equilibrium (or *restricted equilibrium*, as we will say more often) is at the root of the Random First Order Theory (RFOT) of the glass transition that this thesis is based on.

The RFOT posits that the glass transition is, yes, a dynamic phenomenon, but that it has a static origin. This origin comes in the form of a *Free Energy Landscape* (FEL), which is essentially a very rough landscape (think of a golf course, for example) of valleys (minima) separated by ridges (saddles), wherein a single point, representing the glass former, has to navigate towards the bottom of the lowest valley in order to attain equilibration. The dynamics of the system then unfolds as a series of downhill jumps over the ridges (an *activation event*) separated by long persistence times within the valleys (referred to as *metastable states*). The large times needed for activated jumps to take place delay the onset of equilibration and cause the system to behave in a "glassy" manner, and as a result of this, the persistence times are so large that the system is effectively trapped (or equivalently, equilibrated) inside a metastable state for all times which are relevant for experimental and practical purposes.

What is most important about the FEL is that it is a *static* object, in the sense that it is uniquely determined by the equilibrium properties of the system, with no dynamics or time in play. Despite the fact that it prominently affects the dynamics of the glass former, it can be in principle studied with suitable static tools. This scenario opens the possibility that the whole phenomenology of glass could be in principle described by focusing on the study of the valleys (minima) that the system is trapped into during the time regime before equilibration, when the glass exists. In particular, since the system is equilibrated within a metastable state, one could in principle construct a *restricted thermodynamics* by defining a Gibbs measure which only accounts for the micro-configurations which are visited by the system as it vibrates inside this single minimum. From such a measure one could then compute a partition function, a thermodynamic potential, and finally, physical observables.

Such a construction is referred to as *State Following* construction within the theory of generic systems (not only structural glasses) with a rough FEL and a consequent RFOT-like behavior. In this thesis we present and apply this construction to a realistic model of glass former, namely Hard Spheres (HS). We show how it allows to construct a fully analytic theory of glass, entirely from first principles, without the need to resort to dynamical tools; we show how it allows to obtain results for physical observables which are in agreement with the established phenomenology of glasses, and we show how it is also able to provide new insights into, and predictions about, the nature of the glass phase (Fig. 1.1).

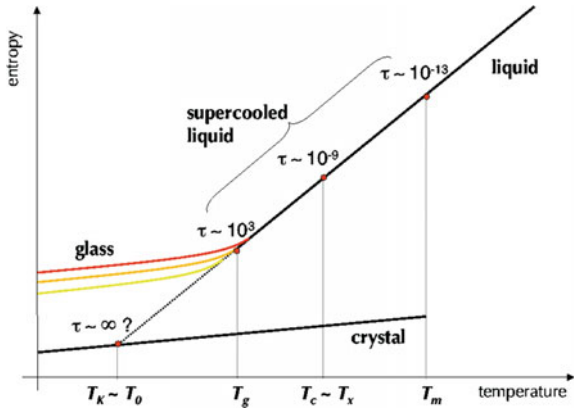

Fig. 1.1 The equations of state of a prototypical glass former. We can distinguish the crystalline branch, the supercooled branch and, in color, the various metastable glass branches. As a guide, in this thesis we will mainly focus on cooling protocols wherein one moves down the supercooled branch and then into the glassy branches, down to $T = 0$. We will not be concerned with the deeply supercooled branch *(dashed line)*. Reprinted from [1]

1.2 The Glassy Slowdown

Most liquids (although not all of them [1]) crystallize upon cooling at a certain *melting temperature* T_m (see Fig. 1.1). However, it is always possible, employing some caution, to *supercool* a liquid below its melting point, avoiding crystallization and producing a *supercooled liquid*.

There are multiple ways to accomplish this. In experiments and industrial applications, one usually cools the liquid fast enough that the nucleation and growth of the crystal take place on times much longer that the experimental time t_{exp} at which measurements are performed. In simulations, the crystal is usually "killed" by introducing polydispersity, i.e. by considering a liquid whose constituents can have different physical shapes (for example spheres with different diameters), so that an ordered, crystalline arrangement of the particles is inhibited. We do not delve into this issue and refer the reader to the detailed discussion of [1].

Once one has managed to obtain a supercooled liquid, it is possible to lower the temperature further, always minding the possibility of crystallization. On doing so, one can then observe a dramatic increase of the relaxation time (we denote it as τ_R) (see Fig. 1.2) over a fairly short range of temperature. Besides this sharpness, this sudden growth is also impressive for its generality: it manifests in systems that range from atomic liquids, to molecular ones, to colloidal compounds and even metallic alloys [2]: any liquid can form a glass if supercooled fast enough [3]. This is already a hint to the fact that the glassy slowdown is a fairly general phenomenon, independent of the actual nature of the glass former under consideration.

We remind the reader that the relaxation time can be defined in terms of the viscosity by Maxwell's relation [1, 4]

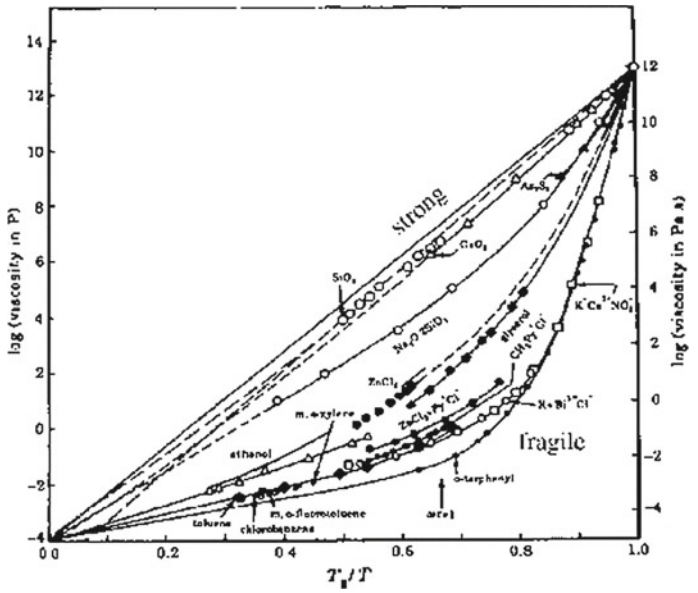

Fig. 1.2 Angell's plot. When the (T/T_g) ratio is reduced by just one half, the most fragile glass formers show an increase of the viscosity (and thus the relaxation time) of almost 16 decades, and the viscosity of the strongest ones increases anyway of about 10 decades. This stunningly sharp growth is one of the most impressive phenomenons in all of low energy physics. Reprinted from [1]

$$\eta = G_\infty \tau_R, \tag{1.1}$$

(where G_∞ is the infinite frequency shear modulus) so that the glass former becomes more and more sluggish as the temperature is lowered. This relation is useful since it allows us to pass from a subtle observable like τ_R to a much more tangible physical property like the viscosity.

1.2.1 The Calorimetric Glass Transition

When the viscosity of a liquid is so high, its ability to flow is severely hampered: it takes a time of order τ_R to relax any excitation (for example shear) the glass former is submitted to. This means that on experimental timescales $t_{exp} < \tau_R$ the glass former will effectually respond to an external perturbation as if it were an elastic solid, i.e. it will present a *shear stress* proportional to the strain [4]

$$\sigma = G_\infty \gamma. \tag{1.2}$$

Indeed, if we simply define a solid as any substance that has an elastic response, the glass former is effectively a solid on timescales such that $t_{exp} < \tau_R$. We stress the fact that this has absolutely nothing to do with the glass transition per se. The fact that a liquid can respond to shear like a solid on short enough timescales is completely general: solidity is indeed a timescale-dependent notion [5]. However, if we put this together with the glassy slowdown, we see that the time we would have to wait to see a liquid-like response to shear becomes rapidly so large that it becomes effectively impossible to do so. When this happens, we get the *calorimetric glass transition*, defined as the point where the equilibration time of the glass former becomes longer than the experimental time, thereby making it a solid from the point of view of the experimentalist. We have then the following implicit definition for the calorimetric glass transition temperature T_g

$$\tau_R(T_g) \equiv t_{exp}. \tag{1.3}$$

This definition of T_g is the one we are going to follow in the rest of this thesis. However, it can be immediately seen that this definition has a problem, namely the fact the t_{exp} depends on how our particular experiment (i.e. our *protocol*) is designed. It is actually more correct to talk about glass transition temperatures, with a plural; but in order to establish a standard, the convention is to set t_{exp} to 10^2 (sometimes 10^3) seconds.[1] This corresponds to having for the viscosity

$$\eta(T_g) \simeq 10^{13}\,\text{Poise}, \tag{1.4}$$

To put this number into perspective, water has a viscosity of about 0.01 Poise, and honey's is about between 20 and 100 Poise. A 10 cm tall cup containing a liquid with a viscosity of 10^{13} Poise would take about 30 years to empty itself [3], so this value corresponds by all reasonable standards to a solid-like response.

The definition of T_g allows us to better appreciate the growth of τ_R at the onset of the glassy slowdown. We can plot on a logarithmic scale the viscosity versus the ratio T/T_g for various glass formers. What we get is the plot in Fig. 1.2, called *Angell's plot* [2]. From Angell's plot we can clearly see that the growth of the viscosity (and so of τ_R) is at least exponential in T, and for some glass formers is even sharper. This is remarkable especially if one considers that the increase of the viscosity at the melting point T_m is much milder [1].

The definition of the calorimetric glass transition also allows us to introduce a problem which underlies the physics of glasses in general: namely the fact that everything has to be defined in a very anthropocentric way. It is true, as discussed in [1], that the increase of τ_R is so sharp that the actual value of t_{exp} doesn't effectively change matters. But this does not deny the fact that the only reason why we talk about a calorimetric glass transition lies in the fact that we are not patient (or long-lived, for that matter) enough to observe the equilibration of the glass former below T_g. One

[1] Indeed, the increase of τ_R is so sharp that the actual choice of t_{exp} does not make much of a difference.