A mean field theory of the glass transition and of jamming of grains and colloids (hard spheres and harmonic spheres)

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Starting from 2005, in collaboration with G.Parisi, I developed a theory of the glass transition, jamming, and the structure of amorphous packings of hard spheres. This theory is based on a mean field approach, and it led to nice results: its predictions have by now been successfully compared to numerical results obtained by several groups. In the following I will give a short account of the physical problem (A), of our theory (B), and of our recent advances (C).

A. Overview of the physical problem

About 50 years ago, Bernal [Bernal and Mason, Nature 1960] used dense disordered sphere packings as model systems to understand the liquid state, at a time where the statistical mechanics of liquids was still in its infancy. However, while liquid state theory grew as a cornerstone of theoretical physics, no equivalent theory was constructed for disordered packings, because they are a nonequilibrium, amorphous, athermal state of matter—a theoretical challenge overlooked by Bernal. Nevertheless, the idea that jammed materials share deep similarities with dense liquids and glasses remains popular today [Liu and Nagel, Nature 1998]. Besides disordered sphere packings, "jammed matter" might refer to a large class of physical systems, such as glasses, colloidal dispersions, granular matter, powders, porous media. Due to this ubiquity of jammed matter, after the pioneering works of Bernal, a huge amount of precise numerical and experimental data on amorphous sphere packings has become available [e.g. Donev et al., PRE 2005; O'Hern et al., PRL 2002 and PRE 2003; Skoge et al., PRE 2006]. Moreover, the sphere packing problem is related to many mathematical problems and arises in the context of signal digitalization and of error correcting codes, and it has been investigated in detail by the information theory community [see the books by Conway and Sloane, 1993, and Rogers, 1964]. This community obtained many interesting rigorous results, but, for space dimension d > 3, only some not very restrictive bounds have been obtained, and in particular it is still unclear whether the densest packings for d going to infinity are amorphous or crystalline (a likely possibility being that the density of amorphous and crystalline packings scales similarly for large d).

Despite this huge numerical and analytical effort, even a very basic question, namely that of giving a precise definition of amorphous packings, is still matter of passionate debate [Kamien and Liu, PRL 2007; O'Hern et al., PRL 2002; Torquato et al., PRL 2000]. The reason, already outlined above, is that dense amorphous packings of hard spheres are usually produced according to some specific dynamical protocol. Typically one starts from an initial random configuration of the spheres, obtained e.g. by throwing them into a container, and then shake, tap, or agitate in some way the spheres until a jammed structure is found. In numerical simulations, amorphous packings are produced by inflating the particles while avoiding superposition either by molecular dynamics or by introducing some energy cost for overlaps, and minimizing the energy in an attempt to find a zero energy configuration. As a matter of fact, most of these procedures, if crystallization is avoided, lead to a final packing fraction close to 0.64 in d = 3 and to 0.84 in d = 2. These values of density, that are approximately 10% smaller than the values of the ordered close packing, have been called "random close packing density". The main problem is that the algorithms (or procedures) that are used to create such packings are complicated dynamical non-equilibrium procedures. Obtaining analytical results for the properties of the final states requires an analytical solution of such complicated dynamical processes, that is very difficult even in the simplest theoretical models [Krzakala and Kurchan, PRE 2007]. Moreover, a small dependency of the final density on the particular algorithm is observed, indicating that although the properties of the final packings are similar, different algorithms do not lead exactly to the same states.

B. Overview of our research methodology

The main strategy behind the theory is to identify a class of amorphous packings that might be described using *equilibrium* statistical mechanics, that is, in a *static* framework. These packings are defined as the infinite pressure limit of glassy states of hard spheres: such glassy states, if dense enough, are well defined metastable states with very long life times, and should be then correctly described by equilibrium statistical mechanics. The idea of studying amorphous packings as the infinite pressure limit of a metastable state has been already discussed in the literature [e.g. Biroli and Mézard, PRL 2001], and is appealing because it converts a difficult dynamical problem into a much simpler equilibrium problem. Our approach to study glassy states is based on the so-called Random First Order Transition (RFOT) theory of glasses, whose

theoretical foundations were posed in a series of papers by Kirkpatrick, Thirumalai and Wolynes [Kirkpatrick and Thirumalai, PRL 1987; Kirkpatrick and Wolynes, PRA 1987; see Cavagna, Phys.Rep. 2009 for a detailed and recent review]. In this theory the glass transition of particle systems is assumed to be in the universality class of the 1-step Replica Symmetry Breaking (1RSB) transition that happens in some mean-field exactly solvable spin glass models [Gross and Mézard, Nucl.Phys.B 1984]. Under this assumption, the glassy states of realistic finite-dimensional systems can be studied analytically, using equilibrium statistical mechanics by means of density functional theory [Stoessel and Wolynes, JCP 1984] and of the replica trick [Mézard and Parisi, JCP 1999; Monasson, PRL 1995]. The replica method seems to give much better quantitative estimates of the glass transition temperature (or density) and of the equation of state of the glass for Lennard-Jones systems [Mézard and Parisi, JCP 1999]. Remarkably, a class of mean-field hard sphere models have been recently formulated, for which the RFOT scenario is exact [Biroli and Mézard, PRL 2001; Mari, Krzakala and Kurchan, PRL 2009; Tarzia *et al.*, EPL 2004]. These models allowed to test the methodology used here, confirming that it is reliable, at least at the mean-field level.

The replica theory of glasses [Mézard and Parisi, JCP 1999] is based on writing the replicated system as a "molecular liquid", and then use standard tools of liquid theory such as the HNC approximation to compute the properties of this molecular liquid. From this computation, one can extract all the thermodynamic of the glass state. For hard spheres, taking the limit of infinite pressure, one finally obtains the properties of amorphous packings. This approach, therefore, allows to go back from liquid theory to amorphous packing, doing the reverse of the path followed by Bernal in the sixties, and showing that there is indeed an intimate connection between the theory of liquids and that of jammed matter.

The resulting theory [Parisi and Zamponi, RMP 2010] allows to compute several thermodynamic and structural properties of amorphous packings of hard spheres. In particular, their entropy (the so-called "configurational entropy"), their pair correlation function g(r), and some geometrical informations such as the average number of contacts between spheres. All these quantities have been compared with numerical simulations, showing a very good overall agreement, with some particularly striking successes, in particular for the scaling of the g(r) close to contact [Parisi and Zamponi, RMP 2010].

C. Further developments of the theory

A first extension, that was performed in [Biazzo, Caltagirone, Parisi, Zamponi, PRL 2009], is to apply the theory to binary mixtures. This is important since nearly all numerical simulations are performed on binary mixtures. In addition to that, the extension to binary mixtures allow to compute new observables. A particularly interesting example is the following. Amorphous sphere packings are isostatic: the average number of contacts for a sphere is equal to twice the dimension of space (so it is 6 in d = 3). This fact is reproduced by the theory, which is already an interesting result. However, since in monodisperse packings all spheres are equivalent, we can only compare this number between theory and simulation. On the contrary, in binary packings, the average coordination number is 6, but it results from an average of *partial* coordination numbers of large and small spheres. A small sphere has a certain average number of contacts with the other small spheres, and with the large spheres, and viceversa. Therefore, by varying the diameter and concentration ratios of the two species, we can vary continuously the partial coordinations (while the total is always equal to 6) and compare the prediction of the theory with numerical and experimental results. This was done in [Biazzo, Caltagirone, Parisi, Zamponi, PRL 2009], and we found nearly perfect agreement. We could also compute the density of packings as a function of diameter and concentration ratios, which also compares well with numerical and experimental results.

A second extension, that was performed in [Jacquin, Berthier, Zamponi, preprint 2011] is to a system of soft spheres: spheres that can overlap, but at the price of paying an energy cost. This model is often used as a model of soft colloidal systems. Because of the finite energy scales, temperature now plays a role and one has to study the phase diagram in the temperature, density plane. The computation of the low temperature scalings around the jamming density required a major technical improvement of the previous theory, which will be detailed in a forthcoming longer version of [Jacquin, Berthier, Zamponi, preprint 2011]. This extension allowed us to get a complete picture of the jamming phase diagram in temperature and density. In particular, we obtained the scaling of pressure and energy close to the jamming point, and more importantly, the scaling of g(r) close to contact. Since g(r) develops a contact delta peak at the jamming point, one obtains an extremely non-trivial scaling at low temperature and around the jamming point, characterized by non-commuting limits and different scaling functions on the two sides of the transition. These scaling functions have been computed and successfully compared with numerical data. Experiments could be realized in the near future.