

Activity Report

Giacomo Gradenigo

Contents

1	Research area in general	1
2	Out-of-equilibrium statistical mechanics	2
2.1	The fluctuating hydrodynamics of granular fluids	2
2.2	Ratchet effect in an aging glass	3
2.3	Anomalous diffusion	4
2.4	The stochastic Lorentz Gas: Large Deviations and Fluctuation Theorem	5
2.5	The spring-block model: Edwards thermodynamics	6
3	Amorphous order in supercooled liquids and the glass transition	7
3.1	Amorphous surface tension and confined supercooled liquids	7
3.2	Dynamical Heterogeneities and the thermodynamics of glasses	8
3.3	Phase transitions in plaquette models for glasses	9

1 Research area in general

In statistical mechanics there are two main categories of systems with interesting “out-of-equilibrium” properties. On one hand we can find *stationary* non-equilibrium systems: these are all the systems which are kept in a stationary state different from equilibrium by an external driving. This can be a mechanism which continuously provides energy to the system and dissipate the amount in excess, or either a mechanism which favors a continuous flux of matter across the system, like the coupling to reservoirs with different chemical potentials. In this situation a system is said to be out-of-equilibrium because the connection between the microscopic interactions and the macroscopic properties cannot be provided by the Boltzmann statistics, due to the presence of fluxes. The main challenge in the study of driven out-of-equilibrium system is to find out a theoretical scheme which remains general with respect to the several specific mechanisms by which energy or matter can be fed to and taken away from the system.

Another class of systems where interesting out-of-equilibrium phenomena take place are *glassy* systems. Usually in glasses there are no net fluxes between the system and the environment: the Boltzmann statistics is valid. Nevertheless, due to a multivalley “complex” energy landscape, the study of the thermodynamic and dynamic properties of these systems still attract a lot of interest. When suddenly cooled to low temperatures glass-forming materials typically fall “out-of-equilibrium” in the sense that the typical time-scale to reach a stationary state becomes much larger than any available experimental time: macroscopic observables like the temperature of the system become time-dependent. The study of glasses is challenging because the properties of their low temperature phase are still under debate: is the dramatic slowing down experienced by these systems due to an underlying phase transition? The access to the low temperature glass phase is particularly hard (practically impossible) due to the exponential increase of relaxation time: this is one of the reasons why the

investigation of the equilibrium properties within the glass phase is still so challenging.

2 Out-of-equilibrium statistical mechanics

2.1 The fluctuating hydrodynamics of granular fluids

Granular fluids are athermal systems made of mesoscopic beads interacting through inelastic collisions. This kind of systems can be maintained in a fluidized stationary state if some energy injection mechanism is provided, in order to compensate the energy loss due to inelastic collisions. The prototype for granular fluids in numerical calculations and theoretical studies is represented by assemblies of hard spheres which experience mutual inelastic collisions and are kept in a stationary state with random kicks (which can be modeled as a white noise). During the last twenty years, due to a microscopic dynamics which intrinsically breaks the detailed balance (inelastic collisions), granular gases have been a playground for many non-equilibrium statistical mechanics theories. As soon as detailed balance is broken the universal description in terms of the Boltzmann weight comes down and the behaviour of the granular assembly becomes strongly dependent on the energy injection mechanism. Granular fluids are from this point of view a very nice example of the striking difference between equilibrium fluids and out-of-equilibrium active ones. As clearly shown in [1], scale free correlations can be found in out-of-equilibrium systems, in particular in granular fluids, without any need of the special cooperative phenomena that at equilibrium arise only close to critical points. An intriguing point is that in a granular gas the range of correlations depends on the energy injection mechanism exploited to keep the system in a stationary state, as I will explain later on. Within the group of Angelo Vulpiani and Andrea Puglisi in Rome, where I spent the period of my first post-doc (Dec 2009 - Nov 2012), one of the main research themes is the study of the role played by the special out-of-equilibrium correlation present in granular fluids in phenomena like violations of the standard fluctuation-dissipation relation.

For what concern the violations of the fluctuation-dissipation relation in granular fluids, in [2] it has been shown that a point of view alternative to the standard description of aging glass formers is possible. Whereas in glasses the violations of the fluctuation-dissipation relation are usually parametrized with the effective temperature T_{eff} , in granular systems it has been shown that the *integrated* response function $\chi(t)$ can be written, without any need of an additional effective temperature, as a linear combination of several correlators $\chi(t) = \sum_{\mu} \alpha_{\mu} C_{\mu}(t)$, which take into account the new correlations that arise between the degrees of freedom of the system in the out-of-equilibrium regime. In the context of dense granular fluids the most important contribution to violations of the fluctuation-dissipation relation comes from *equal-time* correlations between velocities of the particles, which are absent at equilibrium.

The most important contribution that I gave to the group on the study of granular fluids has been a deep investigation on the correlations between particles velocities in the dense regime. In order to study the extent of correlations between particles velocities it is convenient to leave the single particle description in favour of a continuum theory of coarse grained variables, namely temperature, density and velocity fields, which are coupled by the hydrodynamics equations of the model [3, 4, 5]. In this context I realized that the theoretical analysis of [1] was easily adaptable to the model for granular fluids introduced in in [6, 7] by the group of Rome. In the model of [6, 7], which is a monodisperse assembly of 2D disks, between the inelastic collisions the dynamics of each disk is subject to a standard Langevin equation $\dot{v}_i(t) = -\gamma v_i(t) + \xi_i(t)$, where the friction is related to the noise amplitude by the Einstein relation, $\langle \xi^2(t) \rangle = 2T_b \gamma_b$. This was done at variance with the previous standard way to model granular fluids [1], in which the viscous drag was taken equal to zero in the Langevin equation for the dynamics between collisions. The difference is that in [6, 7] the limit of elastic collisions is well defined, because there the single particle energy relaxes to the thermostat temperature T_b , whereas in the model of [1] the single particle energy grows to infinity when the inelasticity of collisions is switched off.

The stability analysis of the linearized hydrodynamics equations of our model showed that there is no instability arising in the packing fraction regime we investigated (namely for packing fraction ϕ in the interval $[0.1 : 0.5]$) [3]. In this interval of packing fractions we also checked the separation between the characteristic times for the evolution of hydrodynamic fields and the microscopic timescale. The conclusion was that the analysis of velocity correlations could be consistently carried on using the linearized hydrodynamic equations plus appropriate noise terms, namely the linearized fluctuating hydrodynamic theory. The most relevant outcome of my theoretical and numerical investigation in this field has been the finding that the correlation of the velocity field, differently from [1] where it is found scale free, decays exponentially with the distance, $\langle v(x)v(y) \rangle \sim \exp(-\xi|x-y|)$ and has an amplitude proportional to the difference $T_b - T_g$ of the two “temperatures” appearing in the equations: the temperature of the thermostat T_b and the granular “temperature” T_g , defined as the average kinetic energy of the granular beads [4]. The existence of equal-time spatial correlations in the velocity field is a genuine non-equilibrium effect: as soon as the collisions become elastic and $T_b - T_g = 0$, the amplitude of such correlations go to zero. A summary of our results is presented in [4]. All the details of the theoretical analysis are reported in [3]. The analysis of velocity correlations in a 2D fluidized granular medium by means of linearized fluctuating hydrodynamics was good enough to well capture the results of numerical simulations, and also of experiments coming from the lab. of A. Puglisi, with results which are thoroughly discussed in [5].

In the granular fluid model introduced in [6, 7], we have found that if one measures the correlation length of the velocity field $\xi(\phi)$ at different packing fractions, and rescales it at every value of ϕ with the appropriate microscopic unit length scale, i.e. the mean free path $\lambda_0(\phi)$, then finds that ξ/λ_0 increases as the packing fraction is increased from $\phi = 0.1$ to $\phi = 0.5$ [3, 4, 5]. It is worthing to notice that is possible to observe this increasing extent of correlation in the velocity field for increasing values of the packing fraction only when the granular gas is coupled to the thermostat introduced in [6, 7]. The same phenomenon could not be observed with the energy injection mechanism of [1]: in this case the correlations have always infinite range at different packing fractions.

2.2 Ratchet effect in an aging glass

Just after the starting of my post-doc in Rome in fall 2009, I took advantage of the experience gained during my Ph.D. on the simulation of glass forming liquids to realize a study in collaboration with A. Puglisi on the realization of the “ratchet” effect in the aging dynamics of a glass former [8]. The “ratchet” effect is well know in the realm of non-equilibrium statistical mechanics [9], and is represented by the rectification of non-equilibrium fluctuations to produce work. There are two very simple but essential ingredients to obtain a ratchet motor [9], which, is worthing to be stressed, is realized without any need of an external driving: the breaking of some kind of spatial symmetry and irreversibility, namely the breaking of detailed balance in the microscopic dynamics. By means of an asymmetric intruder diffusing in an aging glass-formers, we were able to realize the ratchet effect mentioned above, namely to observe a directed motion of the intruder without applying any external force. One of the most striking results presented in [8] is that the the speed of the out-of-equilibrium directed motion of the asymmetric intruder grows in intensity accordingly to the *distance* from equilibrium of the aging host fluid. In the aging regime, in order to “measure” the distance from equilibration, it is usually defined from violations of the fluctuation-dissipation ratio the “effective” temperature T_{eff} of slow modes [10], which is higher than the temperature T of the thermostat coupled to the system. The “distance” from equilibrium is then defined through the ratio $X = T/T_{eff} < 1$, which tends to 1 when the system reaches equilibrium. We found that the speed of the out-of-equilibrium drift of the asymmetric intruder grows with $X^{-1} = T_{eff}/T$, namely the ratchet effect is the more enhanced the more the system is far from equilibrium. This experience has been in my opinion a remarkable example of how ideas well known for stationary out-of-equilibrium systems, like the method to rectify irreversible fluctuations, can be successfully applied to the aging regime of glass-forming liquids.

2.3 Anomalous diffusion

One of the simplest examples of fluctuation-dissipation relations is the Einstein relation. According to the Einstein relation the mean square displacement $\langle x^2(t) \rangle$ of a colloidal particle diffusing in an equilibrium fluid is proportional to its average displacement $\langle x(t) \rangle_F$ when pulled with the external force F , namely one has $\langle x^2(t) \rangle / \langle x(t) \rangle_F = 2/(\beta F)$. Since one knows also that $\langle x^2(t) \rangle = 2Dt$ and $\langle x(t) \rangle_F = F\mu t$, with μ the mobility and D the diffusion coefficient, the Einstein relation reads out also as relation between the mobility and the diffusion coefficient, $\mu = \beta D$. The physical content of the Einstein relation is that one can obtain information on the structure of the host fluid, which are encoded in D , from the response of the system to an external perturbation, i.e. from the mobility μ of a probe pulled with an external force. The validity of Einstein relation is therefore very important for any microrheological study of materials where the physical properties of the host medium are extracted from the transport properties of a probe. A landmark of Fickian diffusion is that not only the unperturbed fluctuations of the probe, but also the fluctuations around the average drift, obey to a *generalized* Einstein relation, namely one has $\langle [x(t) - \langle x(t) \rangle_F]^2 \rangle = \langle [\delta x(t)]^2 \rangle_F = 2Dt$. Let me refer to the unbiased mean square displacement of the probe $\langle x^2(t) \rangle$ as to “equilibrium fluctuations” and to the mean square displacement around the drift in presence of an external force $\langle [\delta x(t)]^2 \rangle_F$ as “out-of-equilibrium” fluctuations. It is well known from the literature that for Continuous Time Random Walks (CTRW) the Einstein relation is not spoiled from the presence of anomalous dynamics [11, 12]. Even when $\langle x^2(t) \rangle \sim t^{2\nu}$, with either $\nu < 1/2$ (subdiffusion), or $\nu > 1/2$ (superdiffusion), for a small applied external field the average drift is in any case proportional to the unbiased fluctuations: $\langle x^2(t) \rangle \sim \langle x(t) \rangle_F$.

When I started to work on the subject of anomalous diffusion in collaboration with A. Vulpiani in Rome, the status of *out-of-equilibrium* fluctuations in Continuous Time Random Walks was still scarcely investigated. Vulpiani brought the attention of the group to the following question: “What happens to *out-of-equilibrium* fluctuations in presence of anomalous dynamics?”, “Do such fluctuations still obey a generalized Einstein relation as in the case of Fickian diffusion?”. While my first step in this kind of problems has been study of the out-of-equilibrium fluctuations for the driven subdiffusive dynamics in some one-dimensional models [13], I gave my major contribution in the three related papers [14, 15, 16]: in [14] suggesting the model and doing both simulations and analytical calculations, in [15, 16] just taking care of the simulations. All of the four papers [13, 14, 15, 16] were devoted to understand the strongly nonlinear interplay between the action of an external forcing and the distribution $P_F(x, t)$ of displacements in the driven anomalous dynamics. The two main results obtained in this series of papers are:

- In the case of anomalous dynamics, either subdiffusive $\nu < 1/2$ or superdiffusive $\nu > 1/2$, the generalized Einstein relation does not hold for the out-of-equilibrium fluctuations, namely $\langle [\delta x(t)]^2 \rangle_F \neq \langle x(t) \rangle_F$.
- In [15, 16] we presented formulas on a general scaling function for the probability of displacements $P_F(x, t)$ in presence of the force F in the case of both subdiffusive and superdiffusive. In particular we studied a Continuous Time Random Walk (CTRW) model with trapping, which is subdiffusive, and the Levy Walk model, which is superdiffusive.

Within the investigation of the CTRW with trapping I came across a special effect: there are situation where both the unbiased mean square displacement $\langle x^2(t) \rangle$ and the drift $\langle x(t) \rangle$ are linear in time, but the out-of-equilibrium fluctuations $\langle [\delta x(t)]^2 \rangle_F$ are superdiffusive. Such a phenomenon received some attention in the recent literature, where it has been found in simulations of viscous liquids close to the glass transition [17] and for a probe particle moving in a crowded environment [18]. Motivated by my interest towards both glass-forming systems and anomalous dynamics, I recently investigated in collaboration with E. Bertin and G.Biroli the anomalous diffusion of a probe particle in a couple of

different Kinetically Constrained Models (KCM). We considered the Fredrickson-Andersen model [19] and the Bertin-Bouchaud-Lequeux model [20]. In this study [21] we find evidence of the same field-induced superdiffusion phenomenon of [18] and we explain why such a mechanism is expected to be a typical one in systems with several and broadly distributed time and length scales. In this forthcoming paper [21] we are also able to provide a clear and intuitive physical explanation of the velocity anomaly observed in [22], which we also find, in terms of the population splitting phenomenon recently investigated in [23, 24].

2.4 The stochastic Lorentz Gas: Large Deviations and Fluctuation Theorem

In the papers [25, 26], realized in collaboration with prof U. Bettolo (Camerino), A. Puglisi (Rome) and prof. H. Touchette (Stellenbosch), I introduced and studied in detail a toy model for granular gases which we called the stochastic Lorentz gas. From the literature a Lorentz gas is known as an ideal gas of point particles which move in the two-dimensional plane colliding elastically with extended obstacles randomly displaced [27]. We attached to our model the adjective “stochastic” because we replaced the immobile obstacles with scatterers of finite mass M and velocities drawn from a Gaussian probability distribution $P(V)$. The collisions between a gas particle and the scatterers are assumed to be a Poisson process, in addition there is a constant force F uniformly accelerating the gas particles between collisions. In practice our model is represented by a particle uniformly accelerated in one dimension and which, at time intervals distributed exponentially, due to an *inelastic* collision with a scatterer attains a new velocity $v' = f(v, V)$, where $f(v, V)$ is a function indicating the collision rule. Due to the constant force F the displacement δx between two collisions is $\delta x = v'\tau + \frac{F}{2m}\tau^2$, with τ the time lag between the two collisions and m the mass of the particle. Although very simplistic, the gas particle moves back and forth on a line where scatterers appear just at the moment of collision and then “disappear”, such a model is an interesting mixture of stochastic and deterministic ingredients [25, 26]. Due to the energy loss from inelastic collisions and the energy gain from the acceleration induced by the force F the gas particles are in stationary non-equilibrium state. For a given choice of the parameters the Boltzmann equation for the velocity probability distribution of the gas particles can be solved exactly (is linear) and the properties of the system determined with great accuracy. For the same choice of parameters exact results are available also for the probability distribution $P(\sigma)$ of the entropy production rate σ : in this situation the interplay between the Fluctuation Relation and other physical properties of the system can be discussed with remarkable precision. If a Large Deviation principle holds for a trajectory of the gas particle which spans a very large time interval t , then the probability distribution of the entropy production rate along this trajectory can be written as $P(\sigma) = e^{-tI(\sigma) + o(t)}$, where the function $I(\sigma)$ is called rate function. Usually, one first computes $I(\sigma)$ and then determines whether the Fluctuation Relation holds or not by looking at the properties of $I(\sigma)$. A sufficient condition for the Fluctuation Relation to hold is the presence of the following symmetry in the rate function: $I(-\sigma) - I(\sigma) = -\sigma$. For the probability distribution $P(\sigma)$ of the stochastic Lorentz gas things happen in the other way around. The main result of [26] is to show from a rigorous calculation of $I(\sigma)$ that while the Fluctuation Relation holds for all the values of σ , the rate function $I(\sigma)$ can be defined only in a finite domain symmetric with respect to zero, namely for $\sigma \in [-\sigma^*, \sigma^*]$. Trying to compute $P(\sigma)$ outside the domain where it can be obtained from a Large Deviations principle, I started recently a collaboration with Satya N. Majumdar which led us in a quite short time to the proof that the two points $-\sigma^*$ and σ^* are two “critical” points where a phenomenon called “condensation of fluctuations” takes place [28]. The term “condensation of fluctuations” is the name attached to situations where in the sum of a large number of random variables almost all the value of the sum is contributed in a non-democratic way by only one of the variables: such a phenomenon has been thoroughly investigated in the mass transport model known as the Zero Range Process [29, 30].

2.5 The spring-block model: Edwards thermodynamics

Since I have started to work at LIPhy in Grenoble (December 2014), my work in collaboration with E. Bertin and J.-L. Barrat has been focused on a model with dissipative dynamics but which can be described with the tools of equilibrium statistical mechanics. This is the spring-block model discussed in my last paper [31]. The spring-block model is a chain of blocks connected by springs and which slide on the horizontal plane. The blocks, when sliding, are subjected to dry friction: they experience a force $f_i = -\mu_d mg \operatorname{sgn}(\dot{x}_i)$ which is always opposed to motion, with μ_d the dynamic friction coefficient and mg the weight of the block. When a block comes to rest it remains stuck at his position due to the dry friction constraint until the modulus of the force exerted on it exceeds the value $mg\mu_s$, where μ_s is the static friction coefficient. If there is no input of energy the spring-block chain, due to dissipation, reaches a mechanically stable configuration where each block is at rest: in such a configuration the force exerted by the springs on each block is smaller than the static friction. This mechanically stable configuration can be also regarded as an absorbing state because, in absence of any external input of energy, the system can never escape this state. By providing periodically an input of energy is possible to make the system jump from one absorbing state to another. The big conceptual question which motivated my work on the spring-block model is the following: is it possible to describe the properties of absorbing states with the tools of statistical mechanics? Since a similar question had been already addressed by Edwards [32, 33, 34, 35] I tried to follow his recipe to compute the partition function \mathcal{Z} for the absorbing states of the spring-block model. In the Edwards theory there is not first principle behind the assumption which allows to compute \mathcal{Z} : theoretical results needs therefore to be compared with molecular dynamics simulations where the absorbing states are sampled by means of a realistic dissipative dynamics. What is worthing to be noticed is that in the simulations we did not used any thermostat or noise: the spring block-model is a driven athermal system. According to the Edwards idea the probability of an absorbing state is provided by the pseudo-Boltzmann factor $e^{-\beta_{Ed}E(\mathcal{C})}\mathcal{F}(\mathcal{C})$, where $E(\mathcal{C})$ is the energy of the absorbing state, $\mathcal{F}(\mathcal{C})$ the function which enforces the mechanical stability constraint and β_{Ed} the inverse of an effective temperature, which in this case is called the Edwards temperature. What is interesting is that the temperature T_{Ed} appears only in the effective theory and not in the real dynamics of the model: the strong assumption of the Edwards approach is that the probability to sample a given absorbing state depends just on his energy and not on the dissipative dynamics used to visit phase space.

In collaboration with E. Ferrero I wrote the code for the molecular dynamics simulations of the model, and I personally took care of doing the simulations and the analytical calculations. I really enjoyed the work on the spring-block model because it was not only focused on a challenging conceptual question, but also gave me the chance to become practical of calculations with transfer matrix techniques for 1D systems.

The study of the spring-block model turned out to be quite successful, because we found a very good agreement between numerical calculations and the exact solution of the theory, which shows the existence of an infinite effective-temperature critical point. We found indeed that correlations diverge when $T_{Ed} \rightarrow \infty$, quite at odd with what happens in ordinary thermal systems, where usually at infinite temperature all the correlations decay on very short distances.

The assumption that absorbing states with the same energy are sampled with the same probability, even if successful in the case just mentioned [31], is not expected to be generally true. For this reason I am investigating at present, still in collaboration with E. Bertin and J.-L. Barrat, what happens to the Edwards effective thermodynamics of the spring-block model if there are *two* sources of dissipation: not only dry friction but also viscous friction [36]. We are interested in understanding whether the hypothesis of the Edwards theory are robust with respect to different mechanisms to dissipate energy. The study of the spring-block model with the tool of Edwards effective thermodynamics is really a promising and rich research line: the possibility to take advantage of equilibrium statistical mechanics tools to study an out-of-equilibrium system would be extremely powerful.

3 Amorphous order in supercooled liquids and the glass transition

3.1 Amorphous surface tension and confined supercooled liquids

One among the most puzzling features of supercooled liquids is that no evident signature of long-range order can be found in proximity of the empirical glass transition temperature T_g , while on the contrary in a narrow interval of temperatures above T_g the relaxation time grows of orders of magnitude. A common opinion in the community of glasses is that amorphous order is indeed present, but needs special correlation functions to be detected. Simple two-points correlation functions like the pair correlation function of simple liquids are not enough to detect it: amorphous order can be detected only using multipoint correlation functions, like the point-to-set correlation function [37, 38, 39, 40, 41].

In the very essence, the scenario to understand the existence of a characteristic length for amorphous order in supercooled liquids is based on the mean-field picture of the glass transition. According to the mean-field picture the supercooled liquid phase is characterized by an exponential number of amorphous configurations with the same free-energy and separated by barriers which grow as the temperature is lowered. If we take as initial condition one of these configurations, after a while and due to thermal fluctuations, a droplet of a new one appears. The nucleation of the new phase is favoured by an entropic gain $\sigma_c R^3 T$, where R^3 is the volume of the droplet and σ_c the configurational entropy (which measures the exponential number of available states), and opposed by a surface cost ΥR^θ , where Υ is the so-called *amorphous surface tension*, while θ is an exponent related to the shape of the interface. The nucleation of the new amorphous phase takes place at the critical length $\ell_{PS} \sim [\Upsilon/(T\sigma_c)]^{1/(3-\theta)}$ where the two contributions balance: ℓ_{PS} is the so-called point-to-set length scale and can be measured via the point-to-set correlation function [38, 39]. Since in the mean-field scenario σ_c vanishes at the ideal glass transition, then ℓ_{PS} is expected to diverge at the glass transition.

During my Ph.D. I worked under the supervision of P. Verrocchio in joint collaboration with A. Cavagna, T. S. Grigera and C. Cammarota. The purpose of my work was to provide some numerical evidence of the ingredients playing a key role in the “phenomenological” Random First-Order Transition (RFOT) theory [37], which is an adaptation of the standard mean-field scenario for the glass transition [54] to realistic glass formers. The work of my Ph.D. was focused on atomistic simulations (Molecular Dynamics, Monte Carlo algorithms, Conjugate Gradient minimization in a multivalley landscape) of a model glass-former, the binary mixture of soft spheres introduced by Grigera and Parisi in [42]. The main result of this collaboration has been the first numerical evidence of the existence of amorphous surface tension Υ between amorphous states [43, 44].

It was during my first post-doc (Rome, 2010-2012), at a time when I was already working mostly on out-of-equilibrium statistical mechanics in collaboration with Andrea Puglisi, that I was able to complete a more refined numerical study on the amorphous surface tension, along with the co-direction (together with A. Cavagna) of the master thesis of Roberto Trozzo on the same argument. By creating and adding the appropriate routines to the C++ object oriented code of T. Grigera (which now is open source [45]), I studied numerically the behaviour of the soft-sphere binary mixture under confinement in a slab geometry. By means of appropriate amorphous boundary conditions [41] the numerical simulations in the slab geometry yielded three main results [41]: 1) allowed us to put on firmer basis the evidence of the amorphous surface tension found in [43, 44]; 2) provided us the evidence that in a supercooled liquids there are *two* lengths which are playing a role, the *point-to-set* correlation length and the *penetration* length; 3) confirmed for a different geometry (the slab geometry) the findings of [39] for the behaviour of the point-to-set correlation function measured in the spherical cavity.

After several numerical papers on the behaviour of supercooled liquids I switched to a more theoretical approach when I worked in Saclay with Giulio Biroli (first year of post-doc in France, 2013). Even though the typical length of amorphous order in glass-forming system, ℓ_{PS} , had been previously

studied only by means of amorphous boundary conditions [37, 39, 40, 50], we were convinced that the ordering of a supercooled liquid on small lengthscales is a general phenomenon, independent from the kind of boundary conditions. Because of that, we decided to work on the analytical model proposed in [50], showing that even completely structureless *random* boundaries are able to trigger the formation of a glass phase in a small spherical cavity [51]: the formation of the glass is solely due to the effect of confinement. According to that we discussed the possible numerical/experimental difficulties in detecting the glass phase induced with *random* boundary conditions. Summarizing, the final important conclusion of [51] is that the result obtained for the first time with amorphous boundary conditions (which are rather special), namely that confinement induces the formation of a glass phase, can be generalized to *any* kind of boundary conditions.

3.2 Dynamical Heterogeneities and the thermodynamics of glasses

One of the distinguishing features of the dynamics in glass-forming liquids is its heterogeneous character: highly immobile regions where the system is frozen in the same amorphous state for a long duration of time coexist with mobile regions where cooperative rearrangements take place. These dynamical heterogeneities can be detected with the so-called four-point correlation function $g_4(\mathbf{r}|, t)$, which was introduced for the first time in [52] and provides information on how much correlated are local rearrangements of the fluid separated by a time lag t and taking place at different positions in the sample. The question which motivated my collaboration also with G. Parisi [53] at the end of my Ph.D. was the following: “Which is the relation between dynamical heterogeneities, which are a finite-dimensional phenomenon, and the mean-field scenario of the Random First-Order Transition for glasses?”. I spent one month in Argentina (Feb 2009) to achieve familiarity with the object oriented C++ code wrote by T.S. Grigera [45] for the Monte Carlo simulations needed for this project.

According to the mean-field scenario of [54] the most important quantity to characterize the glass-transition is the free energy cost $V(q)$ to keep two copies of a supercooled liquid, while they are evolving in time according to two independent stochastic dynamics, at a fixed overlap q , namely at a fixed distance in the phase space. The potential $V(q)$ is the analog for the glass transition of the potential part of Landau free-energy for a phase-transition. When looking at the shape of $V(q)$ at different temperatures, the scenario is identical to the one of a first-order phase transition, with the difference that in the present case the order parameter is q . In the liquid state (high temperature) $V(q)$ has a single “paramagnetic” minimum at $q_0 = 0$: two initial conditions evolving with a different dynamics decorrelate within microscopic times. By lowering the temperature one finds that the supercooled liquid state is related to the birth of a secondary metastable minimum of $V(q)$ in correspondence of a high value of the overlap, $q_1 \sim 1$: the two initial conditions evolving with a different dynamics remains correlated on macroscopic time-scales. When the temperature is lowered further the secondary minimum at q_1 become stable: this is the glass transition where ergodicity is broken.

In [53] we measured for the first time the thermodynamic potential $V(q)$ from the atomistic simulations of a model glass-forming liquid in three spatial dimensions (the binary mixture of soft spheres introduced by T. Grigera and G. Parisi [42]) finding some clear evidence that the potential $V(q)$ behaves upon changing the temperature as expected from the mean-field scenario [54]. My contribution to that paper was in updating the code of T. Grigera for the new simulations and doing the whole analysis on the dynamical heterogeneities in terms of the dynamical structure factor $S_4(k, t)$, i.e. the Fourier transform of the four-point function. It was from this analysis that we get the evidence of the phase-separation between immobile (high q) and mobile (low q) regions accompanying the first-order like behaviour of $V(q)$ [53].

3.3 Phase transitions in plaquette models for glasses

The biggest challenge ever related to the problem of the glass transition is to find a system in finite spatial dimensions and with finite range interaction for which the mean-field scenario of the Random-First Order Theory is verified. For what concern finite-dimensional models a lot of attention has been attracted by Kinetically Constrained Models (KCM) [55]: these are models with a glassy dynamics but where the thermodynamics is trivial, i.e. there are no transitions at finite temperature. Is the scenario proposed by KCMs, where just the dynamics is important, alternative to that of RFOT theory or it is just a complementary description of the same kind of phenomenology? Motivated by this question I worked with Silvio Franz on a two-dimensional lattice spin model known as the Triangular Plaquette Model (TPM), one of the paradigmatic models among KCM [57, 58]. We investigated which kind of perturbations of the Hamiltonian are able to induce a phase-transition in the otherwise trivial thermodynamics of the TPM. For this work on the TPM [56], about which we already received some very good reports from PRE, I wrote the code for the numerical simulations at finite temperature of the model in $D=2$ using the rejection free Bortz-Kalos-Lebowitz Monte Carlo algorithm, which is needed to equilibrate the system at low temperature. I also computed the phase-diagram of the TPM by means of the cavity method: within this approximation the two-dimensional geometry of the model is replaced by the Bethe lattice, namely a locally tree-like geometry where the only loops in the interaction network are of order $\log(N)$. Such structure of the network allows the implementation of a generalized transfer matrix approach, named the cavity approach, by means of which the thermodynamics of the model can be exactly solved. What is surprising of the TPM is the high quality of the predictions on the Bethe lattice, which can be appreciated comparing our results [56] with other very recent works on the same model [59, 60, 61, 62]. I also studied the thermodynamics of the TPM from the point of view of constraint satisfaction problems, using some information theoretical tools already applied with success to the study of systems with a glassy thermodynamics in [63]. From the recent renewed interest on plaquette models [59, 60, 61, 62] in the glassy community, it really looks like that the work that I realized in collaboration with Silvio Franz and co-supervising his master student Stefano Spigler will have some importance in the next years.

References

- [1] T. P. C. van Noije, M. H. Ernst, E. Trizac, and I. Pagonabarraga, *Phys. Rev. E* **59**, 43264341, April 1999.
- [2] A. Puglisi, A. Baldassarri, A. Vulpiani *J. Stat. Mech.* (2007) P08016.
- [3] G. Gradenigo, A. Sarracino, D. Villamaina, and A. Puglisi, *J. Stat. Mech.* **8**, August 2011.
- [4] G. Gradenigo, A. Sarracino, D. Villamaina, and A. Puglisi, *Europhys. Lett.* **961**, October 2011.
- [5] A. Puglisi, A. Gnoli, G. Gradenigo, A. Sarracino, D. Villamaina *J. Chem. Phys.* **136**, 014704 (2012)
- [6] A. Puglisi, V. Loreto, U. Marini Bettolo Marconi, A. Petri, and A. Vulpiani, *Phys. Rev. Lett.* **81**, 3848 (1998).
- [7] A. Puglisi, V. Loreto, U. Marini Bettolo Marconi, and A. Vulpiani, *Phys. Rev. E* **59**, 5582 (1999).
- [8] G. Gradenigo, A. Sarracino, D. Villamaina, T. Grigera, A. Puglisi, *J. Stat. Mech.* L12002 (2010).
- [9] R.D. Astumian, *Science*, **276**, 917, (1997).
- [10] L. F. Cugliandolo, *J. Phys. A (Review Section)* **44**, 483001 (2011).

- [11] E. Barkai, V. Fleurov, Phys. Rev. E **58**, 1296 (1998).
- [12] S. Jespersen, R. Metzler, and H. C. Fogedby, 1999 Phys. Rev. E **59**, 2736 (1999).
- [13] D. Villamaina, A. Sarracino, G. Gradenigo, A. Puglisi, A. Vulpiani, J. Stat. Mech. L01002 (2011).
- [14] G. Gradenigo, A. Sarracino, D. Villamaina, A. Vulpiani, J. Stat. Mech. L06001 (2012).
- [15] R. Burioni, G. Gradenigo, A. Sarracino, A. Vezzani, A. Vulpiani, J. Stat. Mech. P09022 (2013).
- [16] R. Burioni, G. Gradenigo, A. Sarracino, A. Vezzani, A. Vulpiani, Commun. Theor. Phys. **62**, 514 (2014).
- [17] D. Winter, J. Horbach, P. Virnau, and K. Binder, Physical Review Letters **108**, 028303 (2012).
- [18] O. Bénichou, A. Bodrova, D. Chakraborty, P. Illien, A. Law, C. Mejía-Monasterio, G. Oshanin, and R. Voituriez, Phys. Rev. Lett. **111**, 260601 (2013).
- [19] G. H. Fredrickson and H. C. Andersen, Phys. Rev. Lett **53**, 1244 (1984).
- [20] E. Bertin, J.-P. Bouchaud, F. Lequeux **95** , 015702 (2005).
- [21] G. Gradenigo, E. Bertin, G. Biroli, *in preparation*.
- [22] P. Illien, O. Bénichou, G. Oshanin, and R. Voituriez, Phys. Rev. Lett. **113**, 030603 (2014).
- [23] J. Schulz, E. Barkai, R. Metzler Phys. Rev. Lett. **110**, 020602 (2013).
- [24] J. Schultz, E. Barkai, R. Metzler Physical Review X, 4, 011028 (2014)
- [25] G. Gradenigo, U. Marini Bettolo Marconi, A. Puglisi, A. Sarracino, Phys. Rev. E **85**, 031112 (2012).
- [26] G. Gradenigo, A. Sarracino, A. Puglisi, H. Touchette, J. Phys. A: Math. Theor. **46**, 335002 (2013).
- [27] L. A. Bunimovich, Ya. G. Sinai, Commun. Math. Phys. **78**, 479-497 (1981).
- [28] G. Gradenigo, S. N. Majumdar, *in preparation*.
- [29] S. N. Majumdar, M. R. Evans, R. K. P. Zia, Phys. Rev. Lett. **94**, 180601 (2005).
- [30] M. R. Evans, S. N. Majumdar, R. K. P. Zia **123**, J. Stat. Phys. **123**, 357 (2006).
- [31] G. Gradenigo, E. Ferrero, E. Bertin, J.-L. Barrat, Phys. Rev. Lett. **115**, 140601 (2015).
- [32] S. F. Edwards and R. B. S. Oakeshott, Physica A **157**, 1080 (1989).
- [33] A. Mehta and S. F. Edwards, Physica A **157**, 1091 (1989).
- [34] S. F. Edwards and C. C. Mounfield, Physica A **210**, 279 (1994); Physica A **210**, 290 (1994).
- [35] S. F. Edwards and D. V. Grinev, Phys. Rev. E **58**, 4758 (1998).
- [36] G. Gradenigo, E. Bertin, J.-L. Barrat, *in preparation*.
- [37] J-P. Bouchaud and G. Biroli. J. Chem. Phys. **121**, 15, 73477354, (2004).
- [38] A. Cavagna, T. S. Grigera, P. Verrocchio, Phys. Rev. Lett. **98**, 187801 (2007).
- [39] G. Biroli, J.-P. Bouchaud, A. Cavagna, T. S. Grigera, P. Verrocchio, Nature Physics **4**, 771-775 (2008).

- [40] L. Berthier, W. Kob, Phys. Rev. E **85**, 011102 (2012).
- [41] G. Gradenigo, R. Trozzo, A. Cavagna, T. S. Grigera, P. Verrocchio, J. Chem. Phys. **138**, 12A509 (2013).
- [42] T. S. Grigera, Giorgio Parisi, Phys. Rev. E **63**, 045102(R) (2001).
- [43] C. Cammarota, A. Cavagna, G. Gradenigo, T. S. Grigera, P. Verrocchio, J. Stat. Mech. L12002 (2009).
- [44] C. Cammarota, A. Cavagna, G. Gradenigo, T. S. Grigera, P. Verrocchio, J. Chem. Phys. **131**, 194901 (2009).
- [45] Tomas S. Grigera, Computer Physics Communications **182**, 2122–2131 (2011).
- [46] L. Berthier, P. Charbonneau, S. Yaida, arXiv:1510.06320.
- [47] S. Yaida, L. Berthier, P. Charbonneau, G. Tarjus, arXiv:1511.03573.
- [48] D. A. Martin, A. Cavagna, T. S. Grigera, Phys. Rev. Lett. **114**, 225901 (2015).
- [49] V. Krakoviack, arXiv:1511.03408.
- [50] S. Franz, A. Montanari, J. Phys. A: Math. Theor. **40**, No 11 F251-F257 (2007).
- [51] C. Cammarota, G. Gradenigo, G. Biroli, Phys. Rev. Lett. **111**, 107801, (2013).
- [52] C. Donati, S. Franz, G. Parisi, S. C. Glotzer, J. Non-Cryst. Solids 307 - 310 (2002).
- [53] C. Cammarota, A. Cavagna, I. Giardina, G. Gradenigo, T. S. Grigera, G. Parisi, P. Verrocchio, Phys. Rev. Lett. **105**, 055703 (2010).
- [54] S. Franz and G. Parisi, Phys. Rev. Lett. **79**, 24862489 (1997).
- [55] Juan P. Garrahan, P. Sollich, C. Toninelli, *Kinetically Constrained Models*, chapter in book *Dynamical heterogeneities in glasses, colloids, and granular media*, Oxford (2011).
- [56] S. Franz, G. Gradenigo, S. Spigler, arXiv: 1507.05072.
- [57] M. Newman and C. Moore, Phys. Rev. E **60**, 5068 (1999).
- [58] J.P. Garrahan, M.E.J. Newman Phys. Rev. E **62**, 7670-7678 (2000).
- [59] J.P. Garrahan, Phys. Rev. E **89**, 030301(R) (2014).
- [60] R. Turner, R.L. Jack, J.P. Garrahan, Phys. Rev. E **92**, 022115 (2015).
- [61] Robert L. Jack, Juan P. Garrahan, arXiv:1508.06470.
- [62] Giulio Biroli, Gilles Tarjus, Marco Tarzia, arXiv: arXiv:1512.04720.
- [63] M. Mezard, F. Ricci-Tersenghi, R. Zecchina, J. Stat. Phys. **111**, 505 (2003).
- [64] L. Berthier, D. Chandler, J.-P. Garrahan, Europhys. Lett. **69** (3), 320-326 (2005).
- [65] R.-L. Jack, D. Kelsey, J. P. Garrahan, and D. Chandler, Phys. Rev. E **78**, 011506 (2008).
- [66] C. Toninelli, G. Biroli, J. Stat. Phys. **130**, 83-112 (2008).
- [67] C. Toninelli, G. Biroli, Euro. Phys. J. B **64**, 576 (2008).
- [68] V. Narayan, S. Ramaswamy, N. Menon, Science **317**, 105 (2007).

- [69] I. S. Aranson, A. Snezhko, J. S. Olafsen, J. S. Urbach, *Science* **320**, 5876 (2008).
- [70] N. Kumar, H. Soni, S. Ramaswamy and A. K. Sood, *Nat. Commun.* **5**, 4688 (2014).
- [71] K.-D. Nguyen Thu Lam, M. Schindler, O. Dauchot, *New J. Phys.* **17**, 113056 (2015).
- [72] W. T. Kranz, M. Sperl, A. Zippelius, *Phys. Rev. Lett.* **104**, 225701 (2010).
- [73] I. Gholami, A. Fiege, A. Zippelius, *Phys. Rev. E* **84**, 031305 (2011).
- [74] W. T. Kranz, M. Sperl, A. Zippelius, *Phys. Rev. E* **87**, 022207 (2013).
- [75] L. Berthier, J. Kurchan, *Nature Phys.* **9**, 310 (2013).
- [76] L. Berthier, *Phys. Rev. Lett.* **112**, 220602 (2014).
- [77] G. Szamel, E. Flenner, L. Berthier, *Phys. Rev. E* **91**, 062304 (2015).