The discoveries of slowness

Theoretical progresses in off-equilibrium behavior of glassy systems

Giorgio Parisi

Many systems approach equilibrium very slowly. Their equilibration time becomes macroscopic and is sometimes so large that it cannot be measured. Significant progress have recently been made in understanding the collective phenomena that are at the basis of this behavior, especially in structural glasses and spin glasses.

The typical microscopic time scale in condensed matter physics is the picosecond. However sometimes the time to approach equilibrium is much larger (e. g. seconds, years ....). When the gap between the microscopic and the macroscopic time becomes very large, the most common scenarios are the following:

■ There is a localized microscopic process with large activation energy that is responsible for the very large equilibration time.

■ All the localized microscopic processes are fast: there is no single very large energy barrier and the very slow behavior is a collective effect.

The most well understood collective effects happen at a second order phase transition point where there are large-scale excitations that involve a large number of atoms. At the phase transition point the spatial correlation length diverges and at the same time scale becomes very large (critical slowing down): in this situation the characteristic times are much larger than the microscopic time, but usually they still remain microscopic (e. g. they diverge at the critical temperature T_c as $|T–T_c|^{-1.4}$ with a prefactor that is of order of the microscopic time scale).

In other systems the characteristic time diverges much faster (e. g. exponentially) when we approach the transition temperature. In glycerol the characteristic time increases more than 10 orders of magnitude in a narrow temperature range (**Fig. 1**). It is remarkable that the characteristic times are extremely large in the *whole* low temperature phase: in the low temperature regime these systems are always (on human scale) in an off-equilibrium situation: they are often called glasses. In these cases it may be convenient to speak of a collective barrier energy $E(T)$ and to write the characteristic time τ as:

$$\tau \propto \tau_0 \exp\left(\frac{E(T)}{kT}\right) \tag{1}$$

The divergence of τ reflects in a divergence in $E(T)$: indeed the data in **Fig. 1** show an increase of τ that is

much faster than a simple Arrhenius law (i. e. a straight line in the right panel). The divergence in $E(T)$ is a collective phenomenon that must be theoretically explained: we must discover which characteristics correspond to a universal behavior, which are the universality classes.

These systems in the low temperature region are always in an off-equilibrium situation. The experimental data depend crucially on this fact. However the theoretical study of off-equilibrium systems is much more difficult than that of equilibrium systems, since in this case we no longer have a Boltzmann-Gibbs probability distribution. Therefore new tools and ideas are needed.

Glassy systems

Structural glasses

In structural glasses like window glass or wax the viscosity increases by 18 orders of magnitude when we decrease the temperature [1, 2]. In a first approximation the viscosity is the inverse of the characteristic time: we have a spectacular increase of the characteristic time from picoseconds to hours and more (it is difficult to measure characteristic times when they are much larger than one hour). The glass temperature T_g is defined as the temperature where the characteristic time is of the order of one hour. At temperatures less than T_g the system is always at non-equilibrium.

Glasses are usually classified (although there is no sharp separation) as strong glasses or fragile glasses. In strong glasses the viscosity η is proportional to $\exp(B/T)$ (Arrhenius law) and in fragile glasses we have $\eta \propto \exp(B/T–T_K)$ (Volker-Fulcher law).[1)]

The divergence of the characteristic time near T_g

KOMPAKT

■ Significant progress have recently been made in understanding the collective phenomena that are at the basis of systems that approach equilibrium very slowly.

■ An important example is aging in structural glasses and spin glasses.

■ The theoretical predictions, experimental and numerical results lead to generalized fluctuation dissipation relations and the definition of a scale dependent temperature.

■ This makes it possible to consider a space-time picture of the evolution of the system.

Prof. Dr. Giorgio Parisi, Dipartimento di Fisica, Sapienza Università di Roma, INFN, Sezione di Roma I, IPFC – CNR, P.le Aldo Moro 2, I-00185 Roma, Italy – Plenary talk on the occasion of the conferment of the Max-Planck-Medal 2011 at the DPG conference in Dresden.
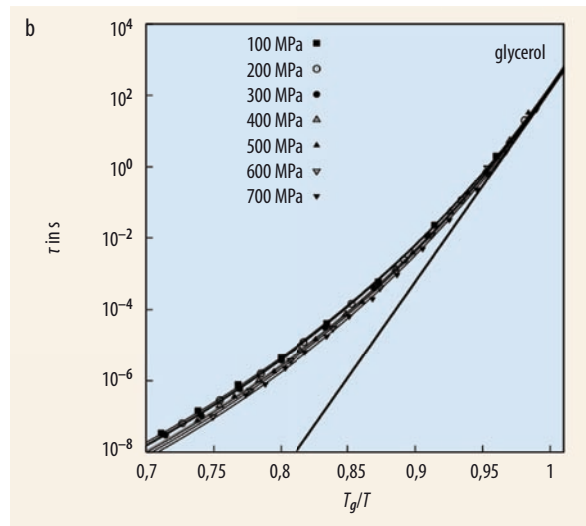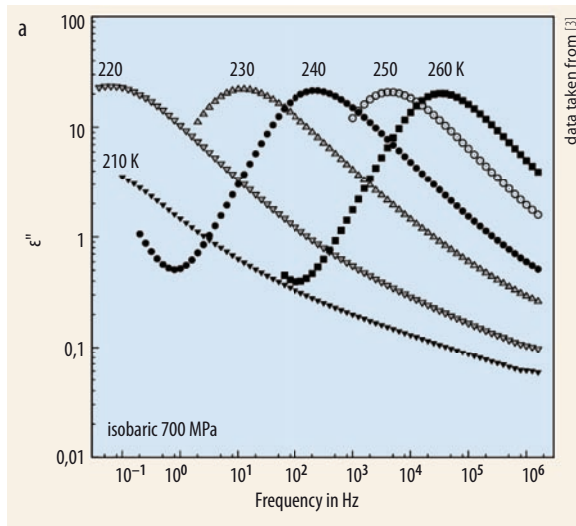
Fig. 1 In glycerol the maximum of the imaginary part of the dielectric susceptibility (as function of the frequency) is proportional to the inverse of the characteristic time (a). The cha-

racteristic time as function of the inverse temperature (at various pressures) increases faster than a simple Arrhenius law (b, straight line).

1) There is a debate whether the Volker-Fulcher law is correct below T_g or if at lower temperatures there must be a crossing to the Arrhenius law. In this note I will assume that the Volker-Fulcher law is correct and that we have a real transition, as suggested from the data in **Fig. 1**.

is usually explained by assuming that the system may have an exponentially large number of local equilibrium states, the dynamics is dominated by collective rearrangements on a scale $\xi(T)$, the length $\xi(T)$ being divergent as a power at T_c [4]. During these collective rearrangements the system must cross a free energy barrier that is proportional to an inverse power of $\xi(T)$. This picture is quite old: the theoretical problem is to find a convincing framework where this scenario can be deduced from first principles and more detailed predictions can be done. The replica approach is particular promising in this respect [5, 6]. A great amount of work has been done constructing soluble models where such a scenario is realized.

Spin glasses

Spin glasses are another prototypical glassy system [7]. Here the disorder is quenched; i. e. it is already present in the Hamiltonian. Spin glasses are realized in nature in many ways, e. g. in the alloys $Fe_5 Au_{95}$. In this case the interaction between two iron spins (RKKY) is proportional to $\sin(2k_F r)/ r^3$.

The simplest model for Ising spin glasses has the Hamiltonian:

$$H_J = \sum_{i,k} J_{i,k}\, \sigma_i \sigma_k \qquad (2)$$

where $\sigma = \pm 1$, i and k are *neighbors*. The J's are random quenched variables (they take both signs). Some bonds are ferromagnetic, some are antiferromagnetic and it is impossible to find a configuration such that $J_{i,k}\, \sigma_i \sigma_k < 0$, $\forall\ i,k$. Finding the ground state is a difficult task (in all senses). Minimal descent brings the system in a local minimum, but there are many local minima (an exponentially large number of minima). From an analytic point of view finding the ground state is an NP-complete problem, i. e. in the worst case any algorithm takes an exponentially large CPU time. We could expect that a physical system will take an incredibly large time to reach equilibrium at low temperatures.

In the 70's John Mydosh and collaborators found the first good experimental evidence of a transition. Deep theoretical studies of spin glass theory started with the Sherrington Kirkpatrick model. This model is conceptually simple and it defines the mean field theory of spin glasses. Unfortunately the theory of spin glasses is difficult. It took a long time to understand this mean-field theory and there are still open problems. At present we can compute analytically nearly all the static properties. The dynamics is more complex. Some quantities are under control, others not. In some lucky

Fig. 2 The analytic results for the SK model (a) agree very well with the experimental data (b) on metallic spin glasses [8].
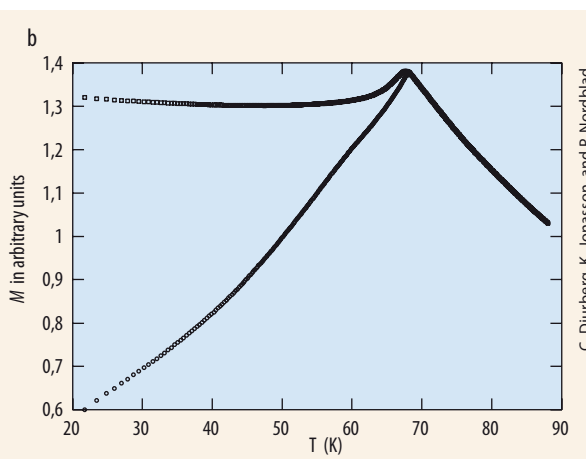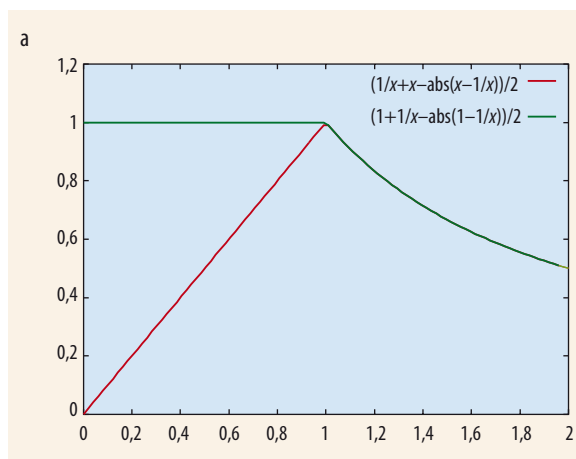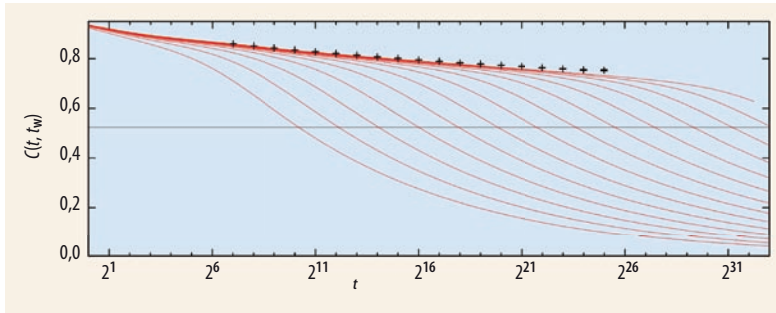
Fig. 3 The two-times correlation function $c(t_w,t)$ in 3–d spin glass. The data correspond to 10^{11} time steps for systems with half a million spins [9]. The different curves correspond to different values of t_w.

cases we can compute dynamic in terms of static (equilibrium) quantities.

One of the main prediction of the mean field (replica) approach is the existence of the different susceptibilities:

- χ_{LR}, i.e. the response within a state, that is observable when one changes the magnetic field at fixed temperature and one does not wait too much.

- χ_{eq}, the true equilibrium susceptibility, that is very near to χ_{FC}, i.e. the field cooled susceptibility, where one cools the system in presence of a field.

The similarities between the pure mean field predictions and the experimental data are striking (**Fig. 2**).

Further predictions of mean field theory

Mean field theory predicts the existence of an exponentially large number of valleys in the free energy landscape. In the simpler case the number of valleys as function of the free energy of the valley F is

$$N(F) \propto \exp[\beta_V (F{-}F_0)] \qquad (3)$$

with $\beta_V < \beta$. This formula recalls $N(E) \propto \exp[\beta (E{-}E_0)]$ that is equivalent to $dS/dE = \beta$, S being the entropy. When we stay in an off-equilibrium situation, Cugliandolo and Kurchan [10] suggested that we can measure two temperatures: one for the configurations inside the valley and one for the valleys, depending on the time scale used for the measurements.

- At short times we measure the standard temperature measured with fast thermometers.
- At long times we measure β_V using slow thermometers that are affected by the jumping between valleys.

The key tool is a generalization of the fluctuation dissipation theorem at equilibrium. At equilibrium we have a relaxation function $R(t)$ and the correlation function $C(t)$ in a system at equilibrium. For a magnetic system, where $M(t)$ is the total magnetization we can define the response functions as $R(t)=\partial M(t)/\partial h$, where h is a field that is added at time zero and $C(t)$ is the correlation of the magnetization, i.e. $\langle M(t)\,M(0)\rangle$. We can obtain a very neat formulation if we eliminate the time t in a parametric way by defining $R(C)$. The fluctuation dissipation theorem states that $dR/dC= -1/T$. Indeed in the text-book formulation one uses the response function $r(t)$ and one writes the equivalent formula:

$$r(t) \equiv \frac{R(t)}{dt} = -\frac{1}{T}\frac{dC(t)}{dt}. \qquad (4)$$

The generalized off-equilibrium fluctuation dissipation relations are similar. We start from an high temperature system and cool the system at the final temperature at time $-t_w$. We define $C(t_w,t)=\langle M(t)\,M(0)\rangle$. In the same way we define the relaxation function $R(t_w,t)$. In the limit $t_w \to \infty$ at *fixed t*, we recover the equilibrium correlation and response functions. The dependence of the correlation $C(t_w,t)$ on both variables is quite complex: in **Fig. 3** we show the correlation $C(t_w,t)$ as function of t at different t_w (in a first approximation
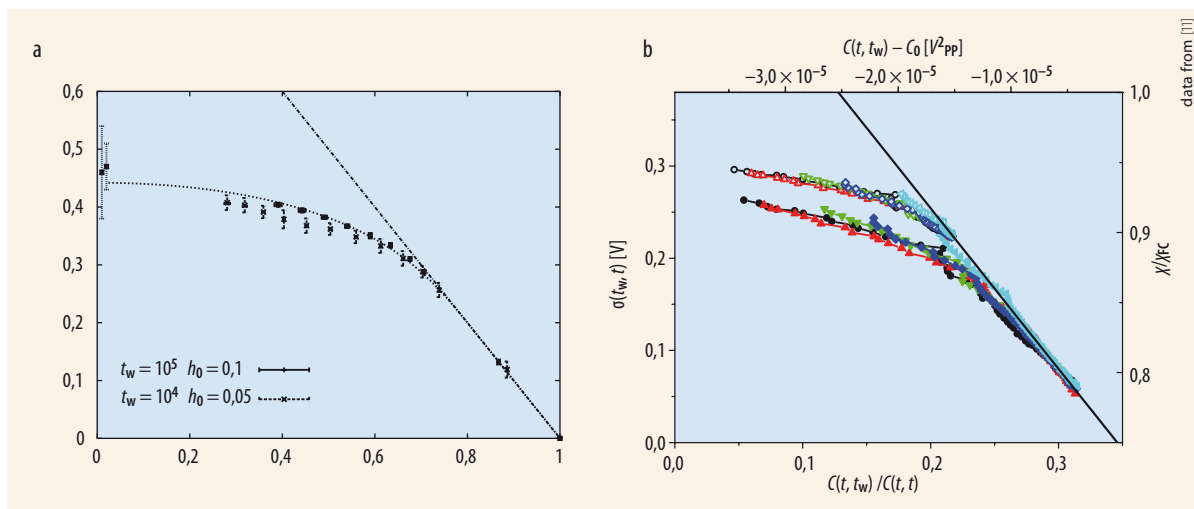

Fig. 4 The relaxation function versus correlations in three dimensional spin glasses. At the left simulations (with an absolu- te theoretical prediction) and at the right experimental data.
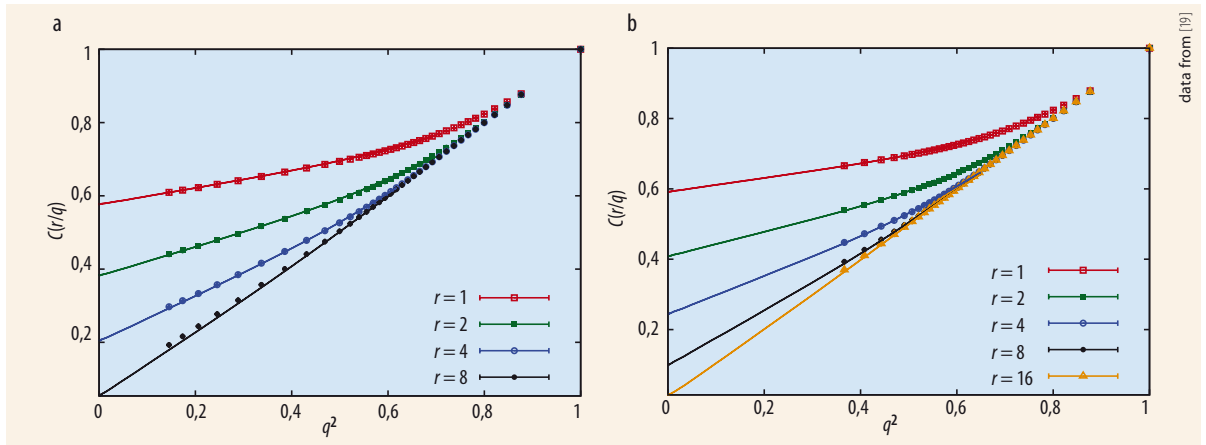
Fig. 5 We compare equilibrated data for the correlations in spin glasses below the critical temperature: in the left panel equilibrium data at $L = 24$ and dynamical data at $t_w = 10^8$; in the right panel static data at $L = 32$ and dynamical data $t_w = 10^{10}$. Solid lines are not fits, but absolute theoretical predictions.

$C(t_w, t) \approx C(t/t_w)$) introducing in this way a time dependent effective temperature. Also in this case for large values of t_w we eliminate the time (t) in a parametric way. The final form of the off-equilibrium fluctuation dissipation relation is

$$\frac{dR}{dC} = -\frac{1}{T(C)} , \qquad (5)$$

where $T(C)$ is an effective temperature. In the simplest two temperatures scenario we have for $C > C_{\text{plateau}}$, $T(C) = T$, while, for $C < C_{\text{plateau}}$, $T(C) = T_V = 1/\beta_V$.

These predictions have been verified both in numerical simulations and in experiments with spin glasses (**Fig. 4**). Similar results and very clear results are obtained for numerical simulations for structural glasses (e. g. Silica), while the experimental situation for structural glasses is more confusing.

The space-time picture

Systematic corrections to mean field can be computed and in this way we obtain information about the evolution of the system in space an time. The main prediction is that at equilibrium in a region of size L there are quite different valleys that have similar free energies. The relative difference of these free energies strongly depends on the boundary conditions.

What we expect if we start the dynamics from an high temperature (random) configuration? The system will be inside one of these valleys if we observe on a scale less than $\xi(t)$ and it will be completely disordered on a scale larger than $\xi(t)$. We expect that the system at large times has dynamic heterogeneities. The dynamics length $\xi(t)$ is the scale of the correlated movement that happens at time t (cooperatively moving regions): i. e. a whole region of size $\xi(t)$ moves from one valley to another valley [12–16].

The presence of dynamic heterogeneities, i. e. of cooperatively rearranging regions, can be well studied in simulations. We have two configurations σ, one at time zero ($\sigma(0)$), one at time t ($\sigma(t)$). The global correlation is $C(t) = V^{-1} \sum_x \sigma(x,0) \sigma(x,t)$. The local correlation is given by $q_D(x) \equiv \sigma(x,0) \sigma(x,t)$. Dynamical heterogeneities correspond to the presence of spatial correlations in $q_D(x)$ at large distances: $C_{2,2}(x,t) = \langle q_D(x) q_D(0) \rangle$. This is exactly what we expect in the case of correlated movement on a large scale.

The presence of long range correlations in the dynamics is the smoking gun for the existence of crucial collective phenomena in the dynamics and strongly supports the need of considering the glass transition as a critical phenomenon that belongs to a quite different universality class from more well understood second order phase transitions. The properties of these long-range correlations are strongly studied these days.

In the case of spin glasses we can also compute theoretically dynamical heterogeneities in an equilibrium ensemble: in other words we can compute some equilibrium correlations that can be shown to be equal to the dynamical correlations. This may be possible if we concentrate our attention on the function $C_{2,2}(x|C) \equiv C_{2,2}(x, t(C))$, $t(C)$ being the inverse of $C(t)$ [17–19]. To this end we consider two replicas in a box of size L as before. The local overlap $q(x)$ between two configurations σ and τ is given by $q(x) = \sigma(x) \tau(x)$. We can also compute the *equilibrium* correlations among $q(x)$ at a given value of the global overlap $q \equiv V^{-1} \sum_x q(x)$. This gives the equilibrium correlations $C(x|q)$ that can be proved [20] to be *magically* equal to the dynamical correlation $C_{22}(x|C)$. A more precise argument can be done in order to take care of finite volume effects in $C(x|q)$ and of finite t_w effects in $C_{2,2}(x,t)$ (**Fig. 5**).

We have just seen that studying dynamical quantities as functions of other dynamical quantities (i. e. eliminating time) is a great simplification: it allows us to obtain absolute predictions for the dynamical heterogeneities. This approach is quite promising and I am sure that it will give rise to new very interesting results and it will also provide a new useful way of presenting data.

Literature

[1] *W. Kob*, Les Houches Session LXXVII on Slow relaxations and non-equilibrium dynamics in condensed matter, edited by *J.-L. Barrat*, *M. Feigelman* and *J. Kurchan* (2003)

[2] *A. Cavagna*, Physics Reports **51**, 476 (2009)

[3] *A. Reiser* and *G. Kasper*, Europhys. Lett. **76** 1137 (2006)

[4] *T. R. Kirkpatrick* and *D. Thirumalai*, Phys. Rev. Lett. **58**, 2091 (1987); Phys. Rev. B **36**, 5388 (1987). *T. R. Kirkpatrick, D. Thirumalai* and *P. G. Wolynes*, Phys. Rev. A **40**, 1045 (1989)

[5] *M. Mézard* and *G. Parisi*, Glasses and replicas, arXiv:0910.2838 (2009)

[6] *G. Parisi* and *F. Zamponi*, Rev. Mod. Phys. **82**, 789 (2010)

[7] *M. Mézard, G. Parisi* and *M. A. Virasoro*, Spin Glass Theory and Beyond, World Scientific, Singapore (1987)

[8] *C. Djurberg, K. Jonason* and *P. Nordblad*, Magnetic Relaxation Phenomena in a CuMn Spin Glass, cond-mat/9810314 (1998)

[9] *F. Belletti* et al., J. Stat. Phys. **135**, 1121 (2009)

[10] *L. F. Cugliandolo* and *J. Kurchan*, Phys. Rev. Lett. **71**, 173 (1993); J. Phys. A: Math. Gen. **27**, 5749 (1994); *L. F. Cugliandolo*, The effective temperature, arXiv:1104.4901 (2011)

[11] *D. Hèrisson* and *M. Ocio*, Phys. Rev. Lett. **88**, 257202 (2002)

[12] *C. Dasgupta, A. Indrani, S. Ramaswamy* and *M. Phani*, Europhys. Lett. **15**, 307 (1991)

[13] *C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole* and *S. C. Glotzer*, Phys. Rev. Lett. **80**, 2338 (1998)

[14] *G. Parisi*, J. Phys. Chem. B **103**, 4128 (1999)

[15] *S. Franz* and *G. Parisi*, Eur. Phys. J. B **8**, 417 (1999)

[16] *G. Biroli* and *J.-P. Bouchaud*, Europhys. Lett. **67**, 21 (2004)

[17] *C. Chamon, M. Kennett, H. Castillo* and *L. F. Cugliandolo,* Phys. Rev. Lett. **89**, 217201 (2002); *H. Castillo, C. Chamon, L. F. Cugliandolo, J. L. Iguain* and *M. P. Kennett,* Phys. Rev. B **68**, 134442 (2003); *C. Chamon* and *L. F. Cugliandolo,* J. Stat. Mech. (2007) P07022; *C. Chamon, F. Corberi* and *L. F. Cugliandolo,* Fluctuations of two-time quantities and time-reparametrization invariance in spin-glasses, arXiv:1105.2949 (2011)

[18] *P. Contucci, C. Giardin, C. Giberti, G. Parisi* and *C. Vernia*, Phys. Rev. Lett. **103**, 017201 (2009).

[19] *R. Alvarez Banos* et al., Rev. Lett. **105**, 177202 (2010)

[20] *S. Franz, G. Parisi, F. Ricci-Tersenghi* and *T. Rizzo*, Properties of the perturbative expansion around the mode-coupling dynamical transition in glasses, arXiv:1001.1746 (2010); Critical behavior of large scale dynamical heterogeneities in glasses: a complete theory, arXiv:1008.0996 (2010); Replica Field Theory of the Dynamical Transition in Glassy Systems, arXiv:1105.5230 (2011)

THE AUTHOR

Giorgi Parisi graduated from Rome University in 1970 under the supervision of Nicola Cabibbo. He worked as researcher at the Laboratori Nazionali di Frascati from 1971 to 1981, with leave of absence from Frascati at New York and Paris. He became full professor at Rome University in 1981. He is now professor of Quantum Theories at the University of Rome I, La Sapienza.

Fotoatelier Konvex