

DISORDERED SYSTEMS

PREDICTING THE ULTRA-SLOW PROCESSES BY PICOSECOND DYNAMICS

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One distinctive feature of the disordered systems is the breadth of their dynamics. It includes picosecond vibrations up to processes, involving the rearrangement of the nanostructure or the diffusive transport, which become observable only over extremely long times, *i.e.* even weeks or years. Numerical simulations and experiments evidence unexpected strong correlations between the picosecond and the ultra-slow dynamics for a wide class of disordered systems. Here we show that the fast wiggling of the atomic or molecular constituents provides a predictive tool of creeping phenomena. The fast predictability of the sluggish dynamics suggests novel routes to tackle complex cutting-edge applicative problems, like the longevity of the data stored in optical media and the long-term stability of biomaterials like food, drugs and vaccines.

1 Introduction

Ultra-slow processes, developing over hours, weeks or much longer times, are common in disordered systems and have important applicative implications. They include the mobility of water or reactants that sets the long-term stability of food [1], biological samples and pharmaceutical products [2], the gas uptake and the chemical aging of semisolid organic aerosol particles affecting the air quality and climate [3], the ionic diffusion in intercalated solids which are used as batteries with high-energy density [4] and the molecular rearrangements occurring in the optical media limiting the longevity of the discs for data storage [5].

Owing to their creeping emergence, the ultra-slow processes are difficult to be characterized. From a more fundamental perspective, the sluggish evolution is often traced back to the phenomenon of the "glass transition", *i.e.* the progressive solidification of a liquid to an amorphous state [6]. In this article we will show that both simulation and experiments unveil the unexpected correlation between the picosecond dynamics and the time scale of the slow molecular rearrangements occurring close to the glass transition (minutes, hours or longer) [7]. To prepare the discussion, a brief outline of the glass transition is given in the next section.

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2 The glass transition: an outline

Daily experience shows that most pure liquids crystallize when sufficiently cooled. However, crystallization may be avoided by diverse routes, *e.g.* by cooling fast enough or by confinement in small volumes, which lead the system to the metastable supercooled liquid state [6]. It is observed that liquids composed of asymmetric molecules are supercooled more easily than those consisting of symmetric molecules. In particular, many macromolecules are virtually incapable of crystallizing due to their global and local irregular structures. A simple empirical indicator of the resistance to freezing is the ratio between the boiling temperature T_b , indexing the cohesive energy, and the melting temperature T_m . It is found that the ratio $T_b/T_m > 2$ for many organic liquids that are easily supercooled. This interrelation is consistent with the effect of molecular asymmetry, decreasing T_m while leaving T_b nearly unaffected as seen, *e.g.*, in isomeric series.

2.1 The cage effect

A phenomenon at the heart of supercooled liquids is the so-called “cage effect”, namely the transient trapping of atoms or molecules by their neighbours¹. **Figure 1** provides an illustration. The trapped particle is not immobilized by the surrounding cage; it undergoes fast irregular vibrations with mean period in the picosecond range and mean square amplitude $\langle u^2 \rangle$ which is determined by the size of the cage. The centre of the vibrational motion is determined by the forces exerted by the neighbouring particles and moves along with the displacement of these particles. In this case, therefore, in contrast to a crystal, one has only temporary and unstable equilibrium positions. After an average time τ_α the cage constraints weaken, due to the rearrangement of the surroundings, and the trapped particle is released. This process is usually referred to as “structural relaxation” and τ_α is named the “structural relaxation time”, a measure of the cage lifetime. The exact definition of τ_α is more involved and is skipped here [7]. After the release, the particle wanders off and then is trapped again.

Figure 2 displays some typical tracks of a mobile particle in a liquid environment at different temperatures. At high temperature, say above the melting temperature T_m , the particle undergoes the usual Brownian random walk (fig. 2, top). Trapping is very short ($\tau_\alpha \approx 10$ ps) and the particle usually does not bounce back when it hits its neighbours. This results in a high self-diffusion coefficient D and a low viscosity η (remind that, according to the Stokes-Einstein law, $D \propto T/\eta$). By lowering the temperature and entering

the supercooled regime, the particle motion becomes more impeded by the cage effect; the random walk is a continuous series of trapping/release events that slows down the particle and increases the viscosity (fig. 2, middle). Looking at the path followed by the particle, it is apparent that marks of a solid (trapping around a position) and a liquid (Brownian random walk) coexist in the typical motion of the particle below T_m . They give rise to a mixed behaviour named “viscoelasticity” which will be discussed in more details in the next section. By lowering the temperature further, the trapping time increases by orders of magnitude and reaches times of the order of minutes, the diffusivity becomes vanishingly small and the viscous flow is strongly hampered (fig. 2, bottom). Conventionally, one defines a “glass transition temperature”, T_g , when $\tau_\alpha = 100$ s. At T_g , by virtue of the Maxwell relation $\eta = G \tau_\alpha$, the viscosity is around 10^{12} Pa s (the elastic modulus G is about 10 GPa). Below T_g , the system undergoes a “structural arrest”; it resembles a virtually immobilized disordered structure, a glass, over times of the order of hours or longer².

The solidification mechanism that we described is not limited to supercooled liquids. It is observed in many other systems, including polymers, bio-materials, colloids and metallic glasses. It must be also pointed out that, in addition to the standard cooling route, the glassy state may be also reached by alternative methods involving, *e.g.*, compression, chemical reactions and solvent evaporation.

2.2 Viscoelasticity

Liquids are fluids; when at rest, they do not sustain a tangential, or shearing, force due to the continuous and irrecoverable change of the particles position. Instead, a deformed solid maintains the shearing forces and the atoms, or molecules, move back to their original positions once the forces are removed leading to a finite elastic modulus G . As discussed in the previous section, viscous liquids are viscoelastic: they exhibit both elastic and viscous characteristics. The rigidity is transient and limited by the structural relaxation. In a low-viscosity liquid ($\tau_\alpha \approx 10$ ps), the high fluidity conceals the elastic behaviour, whereas the reverse happens in an ultra-viscous liquid close to the glass transition ($\tau_\alpha \approx 100$ s).

To better understand the viscoelastic behaviour, let us consider the response of a liquid to an external force applied to the constitutive particles. If a *constant* external force is applied to the particles of a liquid, a particles flow along the direction of the force is observed. If the magnitude of the applied force is sufficiently small, the current of liquid that

¹ For simplicity reasons the discussion is limited to spherical particles. In the case of non-spherical molecules the reorientation of the particles should be also taken into consideration.

² This picture neglects the small-amplitude rattling motion of the particles around their equilibrium position.

arises is seen to be proportional to the applied force; this form of internal friction determines the viscosity of the liquid. An entirely different result is obtained in the case of a *variable* external force that changes so rapidly that its characteristic time is appreciably less than the trapping time τ_α . In the simplest case of a sudden force applied for a short time, the flow mechanism described above does not have time to emerge; the effect of the applied force on the liquid is an elastic deformation just like in a crystal. In this case, in addition to longitudinal elastic deformations of the compression-expansion type one also observes transverse (shear) elastic deformations due to the occurrence of tangential stresses. In most experiments it is more convenient to apply continuously acting oscillatory forces instead of transient forces to observe the viscoelasticity. In the high-frequency limit ($f \gg 2\pi / \tau_\alpha$), solid-like elastic response is observed. In the opposite low-frequency limit ($f \ll 2\pi / \tau_\alpha$), the fluidity of liquids completely masks their elasticity. In the intermediate range ($f \sim 2\pi / \tau_\alpha$), the liquid response to the applied force exhibits both viscous and elastic characteristics.

3 Structural stability criteria

The transition to a glass is usually described as an approach to states with vanishing fluidity. An interesting alternative is offered by recognizing that, on approaching the glass transition, the transient elasticity of viscous liquids is not only more persistent in time but it is also increasing in magnitude. Thus, the increase of the rigidity is a measure of the stability of the disordered microscopic structure. The notion of elastic stability was introduced by Born who investigated the melting of crystals [8]. The crystal would lose its rigidity or "stability" and melt when at least one of the shear moduli vanishes.

Another well-known stability criterion for crystals is the Lindemann criterion which states that melting occurs when the mean-square amplitude of thermal vibrations of atoms, $\sqrt{\langle u^2 \rangle}$ reaches a critical fraction of the nearest-neighbour separation d ($\sqrt{\langle u^2 \rangle} \approx d/10$) [9]. An oversimplified picture

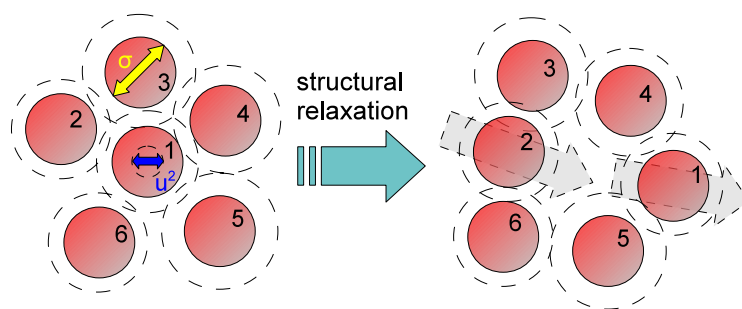


Fig. 1 The cage effect in viscous liquids. Particles, here sketched as spheres with σ diameter, are temporarily trapped by their neighbours. During the trapping period the centre of the particles undergoes irregular fast vibrations with mean square amplitude $\langle u^2 \rangle$. After an average time τ_α the restraint weakens, the trapped particle "1" escapes from the cage and is replaced by a new one, "2".

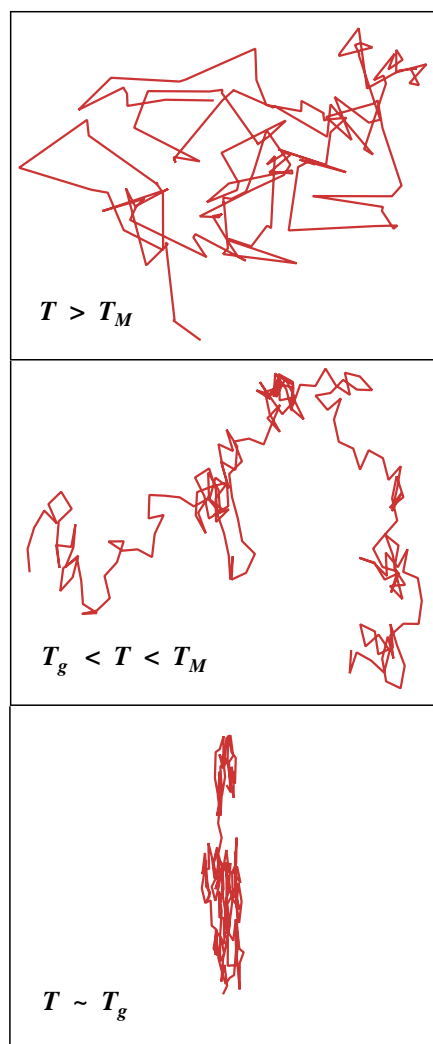


Fig. 2 The paths of the random walk of a particle in a liquid at high temperature (top), in the supercooled regime (middle) and close to the glass transition (bottom). At lower temperatures the particle movement is temporarily restricted by the neighbours. The trapping time τ_α becomes as long as minutes close to the glass transition.

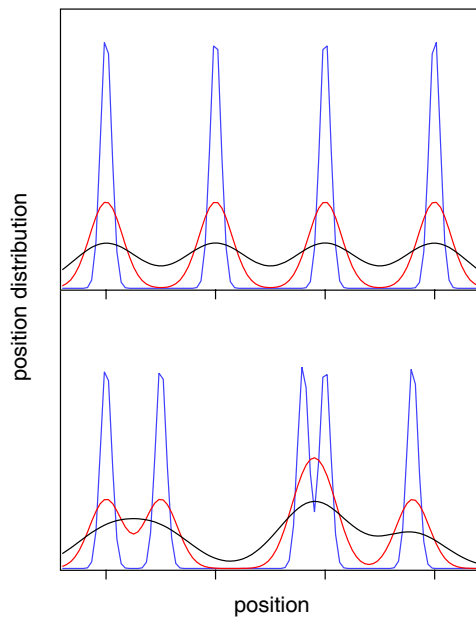


Fig. 3 Distribution of the particles around the equilibrium positions of an ordered (top) and a disordered (bottom) 1D structure subjected to different thermal vibrations due to low (blue), intermediate (red) and high (black) temperature. The blur effect increases with the temperature and masks the equilibrium structure. According to the Lindemann melting criterion, the red and black curves for the ordered structure correspond to unstable states. Numerical simulations suggest extensions of the Lindemann criterion to disordered structures.

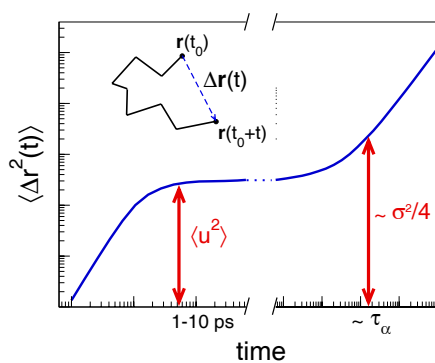


Fig. 4 Time evolution of the mean square displacement of the monomer belonging to a polymer chain. After a short initial displacement, the neighbours cage the monomer which wiggles with mean square amplitude $\langle u^2 \rangle$. The average trapping time is τ_α . Within this lapse of time the displacement is comparable to the monomer radius $\sigma/2$.

of the position distribution due to the thermal vibrations around the equilibrium positions of ordered and disordered structures is presented in fig. 3. One sees that, on increasing the amplitude of the thermal vibrations, the equilibrium structure is progressively blurred. For crystals this effect results in structural instability and melting.

4 Structure lifetime and cage rattling in disordered systems

Numerical simulations and experiments suggest the possibility to extend the Lindemann criterion to viscous liquids [7]. One finds that the mean square amplitude $\langle u^2 \rangle$ of the irregular vibrations in the cage of the neighbours (fig. 1) is a good indicator of the lifetime of the disordered nanostructure τ_α .

Let us focus on the simulations, which considered a liquid of a polymeric linear chains melt. The model is very rough; each chain comprises a series of spherical beads linked by stiff springs. The coarse-grained nature is motivated by the attempt of finding a universal behaviour which is independent of the detailed structure of the molecule. Figure 4 shows the typical time evolution of the mean square displacement (MSD) of one monomer of a tagged polymeric chain. The MSD shows three different regimes:

- At **very short times** the monomer undergoes a ballistic motion, *i.e.* it moves almost freely like in a gas phase, $\langle \Delta r^2(t) \rangle = \langle v^2 \rangle t^2 = 3 k_B T/m t^2$, where v , m , T and k_B are the velocity, the mass of the monomer, the temperature and the Boltzmann constant, respectively.
- At **intermediate times**, the monomer is trapped within the cage formed by its first neighbours and the mean square displacement is almost constant at a value $\langle u^2 \rangle$. The cage lifetime is finite and the monomer escapes after an average time τ_α which is orders of magnitude longer than the picosecond average period of the wiggling motion in the cage. The MSD at τ_α is about the square of the particle radius.
- For **much longer times than the escape time τ_α** , the monomer undergoes diffusive

motion $\langle \Delta \mathbf{r}^2(t) \rangle = 6Dt$, where D is the self-diffusion coefficient³.

Figure 5 summarizes the results of the simulations performed at several densities and temperatures as well as at different number of monomers M per chain and diverse interacting potentials. These results suggest that the cage lifetime τ_α and the mean square wiggling amplitude in the cage $\langle u^2 \rangle$ are strongly correlated. The inset of fig. 5 shows that the correlation holds also in the diffusive regime that develops at much longer times than τ_α ⁴.

The correlation plot of $\log \tau_\alpha$ vs. $\langle u^2 \rangle^{-1}$ is described by a "master curve" which turns out to be a parabola in $\langle u^2 \rangle^{-1}$:

$$(1) \quad \log \frac{\tau_\alpha}{\tau_0} = \beta \langle u^2 \rangle^{-1} + \gamma \langle u^2 \rangle^{-2},$$

where β and γ are constants. A simple model of the structural relaxation in a viscous liquid provides insight into eq. (1) [10, 11]. It assumes that the particle must overcome an energy barrier ΔE in order to escape from the cage. It is found that the barrier is inversely proportional to the wiggling amplitude, $\Delta E \propto k_B T a^2 / \langle u^2 \rangle$, where a is the displacement needed to reach the top of the barrier (fig. 6). Within this simplified model eq. (1) is recovered with $\beta \propto a^2$ and $\gamma = 0$. In a disordered system the particles do not displace by the same amount to escape from their cages. If a proper distribution is introduced, one derives eq. (1) with $\beta \propto \overline{a^2}$ and $\gamma \propto \sigma_{a^2}^2$, where $\overline{a^2}$ and $\sigma_{a^2}^2$ are the average and the variance of the square displacements to overcome the barrier [7].

5 Universal scaling

Are the correlations observed by the simulations supported by the experiments? The answer is positive as is shown in fig. 7

³ After the escape from the cage, the monomer initially displaces very slowly, since it is constrained by the other monomers of the chain. The usual Brownian diffusion manifests at later times when the whole chain starts moving. In a simple liquid the intermediate regime is missing.

⁴ The diffusion coefficient of a short polymer chain is inversely proportional to the chain length M . To remove this dependence, the product DM is considered.

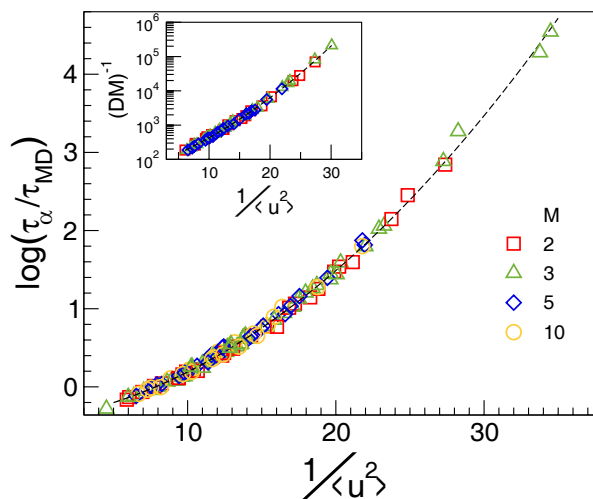


Fig. 5 The high correlation between the average lifetime of the cage (in reduced units) and the inverse of the mean square wiggling amplitude of the monomer in the cage. They are evidenced by the simulation of a polymeric liquid. The dashed line is the master curve given by eq. (1). The average wiggling period is about one time unit τ_{MD} , corresponding to about 1–10 ps, whereas τ_α may be orders of magnitude longer. The inset shows that the correlation holds for the self-diffusion coefficient too.

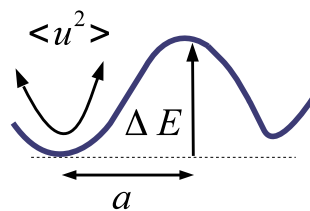


Fig. 6 Simple activated model relating the energy barrier ΔE that the particle must overcome to escape from the cage and the wiggling amplitude. a is the displacement to reach the top of the barrier.

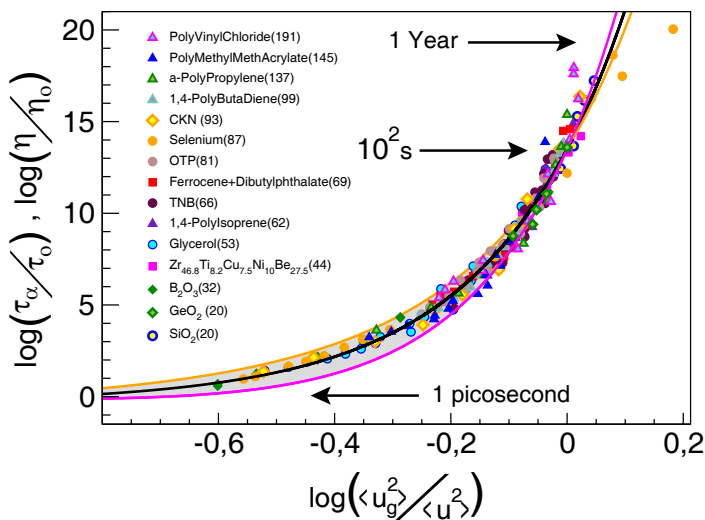


Fig. 7 Experimental evidence of the correlation between the structural relaxation time (or the viscosity η) and the wiggling amplitude for several systems approaching the glass transition. $\langle u_g^2 \rangle$ is the amplitude at the glass transition. The black line is calculated using eq. (1) as drawn by the simulations and recast in terms of the reduced amplitude $\langle u^2 \rangle / \langle u_g^2 \rangle$. Note that the vertical axis spans about eighteen orders of magnitude.

where the structural relaxation time and the viscosity over a range of about eighteen orders of magnitude for a wide set of different systems approaching their glass transition, including polymers, metallic glasses, ionic liquids, tetrahedral liquids⁵, hydrogen-bonded and van der Waals molecular liquids are plotted [7]. Both quantities are clearly correlated to the reduced mean square wiggling amplitude $\langle u^2 \rangle / \langle u_g^2 \rangle$, where $\langle u_g^2 \rangle$ is the amplitude at the glass transition. The scaling is quite effective and the master curve (black line) is calculated using eq. (1) with the same coefficients β and γ obtained by the simulations, and rewritten in terms of the reduced amplitude.

Much of our current efforts are devoted to understand the origin, as well as the limits, of the scaling. In this respect, both the elasticity in polymers and liquids [12] and the connectivity between particles in a model colloidal gel [13] have been addressed.

Acknowledgements

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Dino Leporini

Dino Leporini is associate professor at the Department of Physics "Enrico Fermi" of the University of Pisa. He is interested in the physics of disordered systems, in particular polymers, liquids and liquid crystals, which are studied by Electron Spin Resonance spectroscopy and simulations.

⁵ Tetrahedral liquids exhibit a preference for the formation of tetrahedrally coordinated configurations.

Durante la preparazione di questo numero de IL NUOVO SAGGIATORE, l'INFN (Istituto Nazionale di Fisica Nucleare) ha diramato il comunicato stampa che qui di seguito riportiamo:

L'INFN RIVEDE IL SUO PROGETTO BANDIERA
Pubblicato Mercoledì, 28 Novembre 2012

I risultati della commissione internazionale nominata dal MIUR per il costing review del progetto bandiera SuperB sono stati esaminati ieri dal Ministro della Ricerca che ha voluto discuterne con i vertici dell'INFN e successivamente con quelli del Cabibbolab. Il Ministro ha fatto presente che non erano in discussione l'importanza e la qualità del programma, ma che le condizioni economiche del Paese e i limiti previsti dal Piano Nazionale per la Ricerca, erano incompatibili con i costi del progetto valutati. Il Ministro, mostrando grande disponibilità, ha dato la possibilità all'INFN di proporre progetti, sempre nella tipologia dei "progetti bandiera", compatibili con lo stanziamento previsto inizialmente. Le proposte dovranno essere valutate entro pochi mesi. L'INFN sta quindi vagliando le idee in merito. Tra le possibilità, comunque, verrà esplorata con convinzione l'ipotesi di presentare il progetto per la realizzazione di un laboratorio internazionale finalizzato alla costruzione di una macchina acceleratrice nell'area di Frascati. (http://www.infn.it/index.php?option=com_content&view=article&id=359:bandiera&catid=21:news&Itemid=532&lang=it).

A tale comunicato ha fatto immediatamente seguito, il 29 Novembre, quello del Cabibbolab (<http://www.cabibbolab.it>).

Dato l'interesse scientifico dell'articolo di M. Giorgi e M. Rama su "The Super Flavor Factory SuperB", previsto per questo numero, abbiamo ritenuto di pubblicarlo comunque nella sua stesura originale.

While the present issue of IL NUOVO SAGGIATORE was in preparation, INFN (the Italian National Institute of Nuclear Physics) circulated the following press release:

INFN REVISES ITS FLAGSHIP PROJECT
Published on Wednesday November 28th, 2012

The results of the international commission appointed by MIUR (Ministry of Education, University and Research) for the costing review of the flagship project SuperB have been examined yesterday by the Minister of Research who then wanted to discuss them first with INFN and subsequently with Cabibbolab management. The Minister underlined that neither the relevance nor the quality of the program were brought into question, but that the economical situation of our Country and the limits set forth by the "Piano Nazionale per la Ricerca" (National Research Plan) were incompatible with the evaluated costs of the project. The Minister demonstrated his willingness giving INFN the opportunity to submit other proposals of the same typology as "flagship projects" that should fit the initially foreseen allocation. The proposals shall be evaluated in a few months.

Therefore INFN is weighing up ideas in this respect. Among the possibilities, anyway, the hypothesis of the project for the realization of an international laboratory, having as purpose the construction of an accelerator in the Frascati area, will be firmly considered. (http://www.infn.it/index.php?option=com_content&view=article&id=359:bandiera&catid=21:news&Itemid=532&lang=it).

To this press release immediately followed, on November 29th, that of the Cabibbolab (<http://www.cabibbolab.it>).

Given the scientific interest of the paper by M. Giorgi and M. Rama on "The Super Flavor Factory SuperB", scheduled for this issue, it was considered appropriate to publish it anyhow in its original form.