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.

** Present address: LIPHY, Univ. Grenoble 1, Saint Martin d’Hères, France.
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 \( T_b / T_m \geq 2 \) 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 neighbours\(^1\). 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 \((\alpha^2)\) 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 \( \tau_a \) 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 \( \tau_a \) is named the “structural relaxation time”, a measure of the cage lifetime. The exact definition of \( \tau_a \) 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 \((\tau_i = 10 \text{ ps})\) 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 \( \eta \) (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 \( \tau_i = 10^2 \text{ s} \). At \( T_g \), by virtue of the Maxwell relation \( \eta = G \tau_s \), the viscosity is around \( 10^{12} \text{ Pa s} \) (the elastic modulus \( G \) is about \( 10 \text{ GPa} \)). 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 longer\(^2\).

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 \((\tau_i \approx 10 \text{ ps})\), the high fluidity conceals the elastic behaviour, whereas the reverse happens in an ultra-viscous liquid close to the glass transition \((\tau_i \approx 100 \text{ s})\).

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

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\(^1\) 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 negligibly less than the trapping time $\tau_\alpha$. 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 responses 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...
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 \( \langle \sigma^2 \rangle \) of the irregular vibrations in the cage of the neighbours (fig. 1) is a good indicator of the lifetime of the disordered nanostructure \( \tau_a \).

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, \( \langle \sigma^2 \rangle = \langle v^2 \rangle t^2 = \frac{3}{2} k_B T m t^2 \), 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 \( \langle \sigma^2 \rangle \). The cage lifetime is finite and the monomer escapes after an average time \( \tau_a \), which is orders of magnitude longer than the picosecond average period of the wiggling motion in the cage. The MSD at \( \tau_a \) is about the square of the particle radius.

- **For much longer times than the escape time \( \tau_a \)**, the monomer undergoes diffusive...
motion $\langle \Delta r^2(t) \rangle = 6 D t$, where $D$ is the self-diffusion coefficient$^3$.

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 $\tau_c$ 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 $\tau_c$.$^4$

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

$$\log \frac{\tau_c}{\tau_{c0}} = \beta \langle u^2 \rangle^{-1} + \gamma \langle u^2 \rangle^{-2},$$

where $\beta$ and $\gamma$ 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 $\Delta E$ 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 $\beta \propto a^2$ and $\gamma \propto \sigma _w^2$, where $\sigma _w^2$ and $\sigma _w^2$ 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 $D M$ is considered.
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 liquids\(^5\), hydrogen-bonded and van der Waals molecular liquids are plotted \(^7\). Both quantities are clearly correlated to the reduced mean square wiggling amplitude \((u^2) / (u^2)_g\), where \((u^2)_g\) is the amplitude at the glass transition. The scaling is quite effective and the master curve (black line) is obtained by the simulations, and rewritten in terms of the obtained 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 properties are devoted to understand the reduced mean square wiggling amplitude \((u^2) / (u^2)_g\), where \((u^2)_g\) is the amplitude at the glass transition. The scaling is quite effective and the master curve (black line) is obtained by the simulations, and rewritten in terms of the obtained 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.

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References


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.