Local Motifs and the Rise of Solidity in Deeply Supercooled Liquids

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Introduction. We investigate the role that Locally Favoured Structures (LFS) play in the emergence of the solid-like behaviour of glassy systems in numerical simulations. To do so, we start from extremely cold configurations ($T \sim 0.97 T_g$) and perform a shear experiment testing the zero-temperature limit of a set of rheological properties. We distinguish the more plastic and the more elastic regions and correlate them with the localisation of the LFS.

1. Generating highly **structural** configurations *via* **importance sampling** of **trajectories**

Locally Favoured Structures (LFS) in supercooled liquids are local particle motifs that are energetically favourable and linked to **transient short range** order.

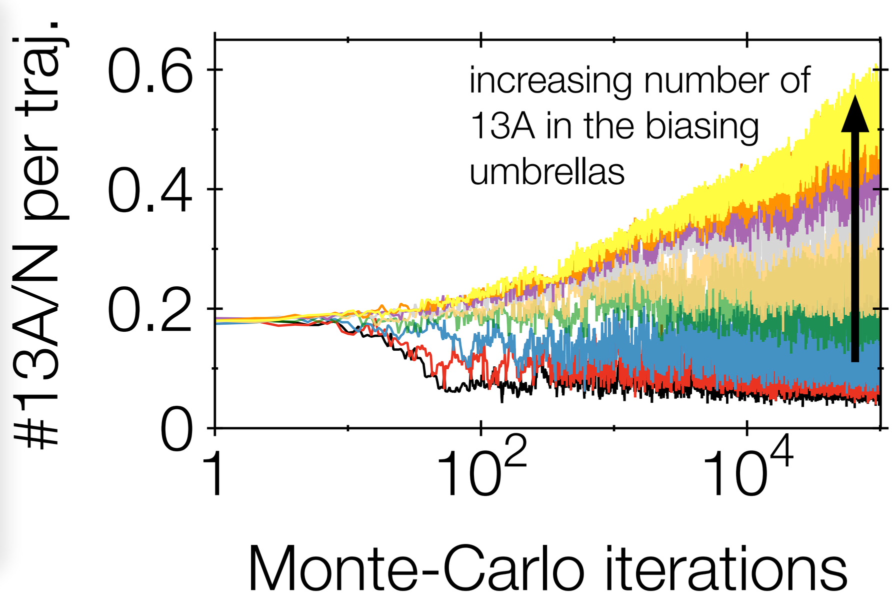


Fig. 1 Sampling trajectories **biased** according to the time-integrated fraction of icosahedral structures 13A for N=512 particles.

We consider a simple binary mixture [1] where icosahedral LFS have been observed. We manage to obtain **high concentrations** of **icosahedra** (13A) via **Transition Path Sampling** (TPS) [2].

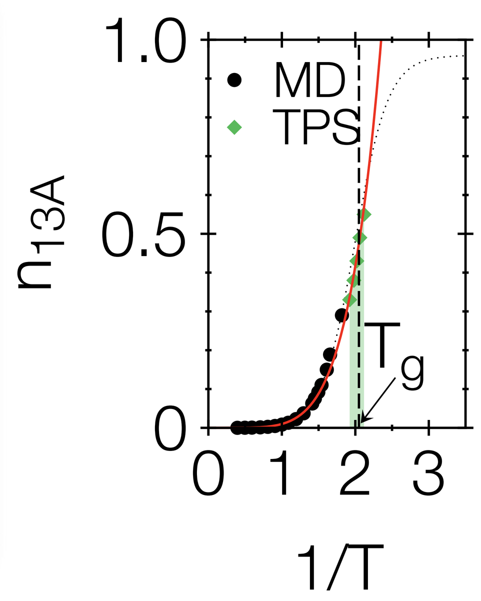


Fig. 2 LFS-rich phases can be interpreted as very **cold** samples. The corresponding temperature can be extrapolated from the icosahedra growth law determined via standard Molecular Dynamcis [2].

2. Probing the mechanical response in the **Athermal Quasistatic Limit**

The relation between solidity and icosahedral order is probed through a rheological test: the sample is sheared at T=0 and performs a succession of **affine deformations** (at constant shear rate) and potential energy **minimisations** [3].

$$T = 0$$
$$r_{ix} \to r_{ix} + r_{iy}\delta\gamma$$
$$r_{iy} \to r_{iy}$$
$$r_{iz} \to r_{iz}$$

Eq.1 The equations of motion are fully **deterministic** with a constant shear rate $\dot{\gamma}$.

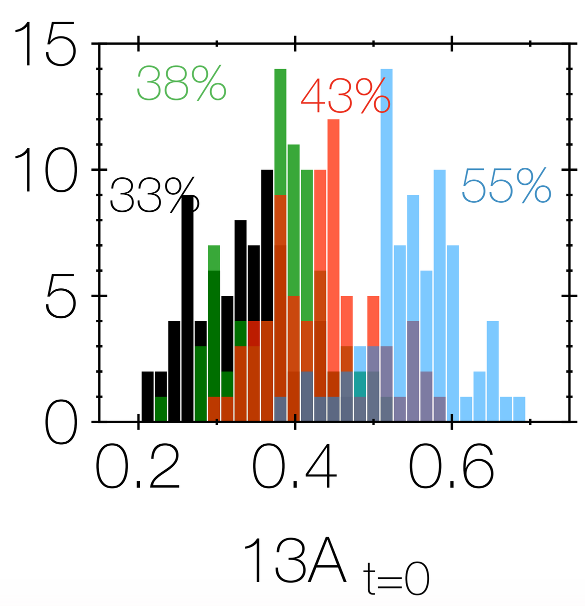


Fig. 3 The TPS **umbrellas** provide consistent **ensembles** of configurations characterised by large values of the concentration of icosahedra.

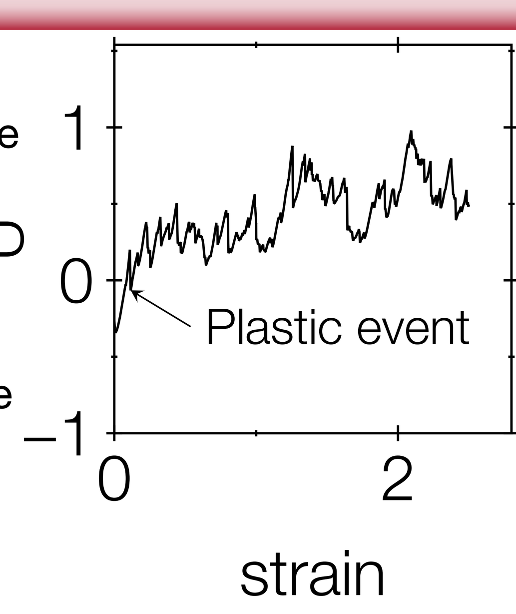


Fig. 4 The **potential** energy for different values of the strain illustrates the succession of **plastic** events.

3. More **icosahedral** structures enhance the **yield stress** and the **elastic modulus**

While the energy minimisation initially optimises the fraction of 13A, the shearing protocol leads to a gradual fluidification.
This is **strongly dependent** on the initial fraction of icosahedra.

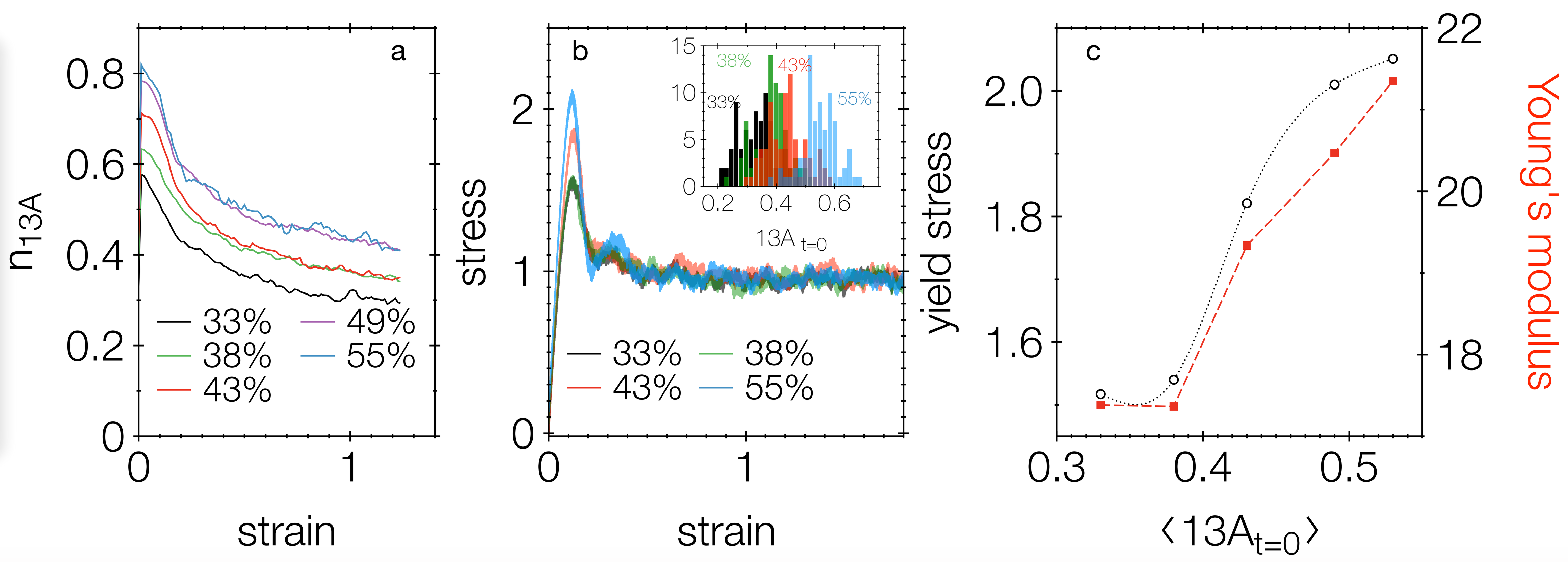


Fig. 5 Fluidification of the the initial configurations: a) decrease of the fraction of icosahedral particles; b) stress-strain curves and c) related measurements of yield stress (stress-peak) and Young's modulus for different initial average concentrations of LFS.

4. The **plastic** events occur **outside** the icosahedral clusters

Dynamic information from the **non-affine displacements** [4] and static features from the **mode analysis** [5] anti-correlate with the location of the icosahedral clusters.

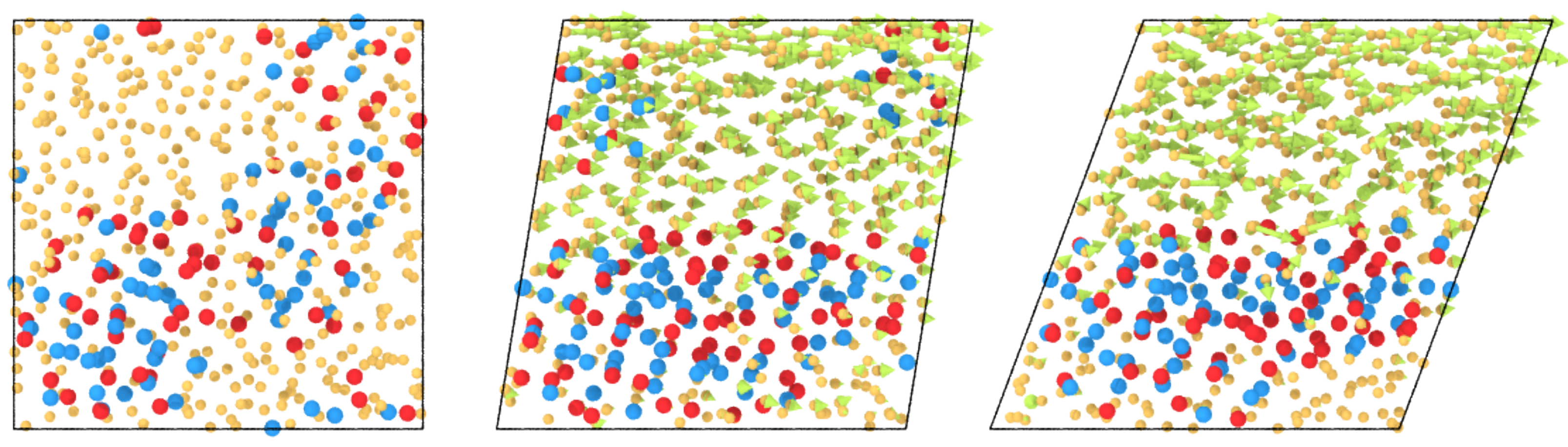


Fig. 8 Displacement field and icosahedral order: shear-banding can be observed, with much larger mobility in the regions not occupied by the LFS structure.

Fig. 9 Differences in the averages of Dmin, the local deviation from uniform strain [4] between icosahedra and the rest of the sample.

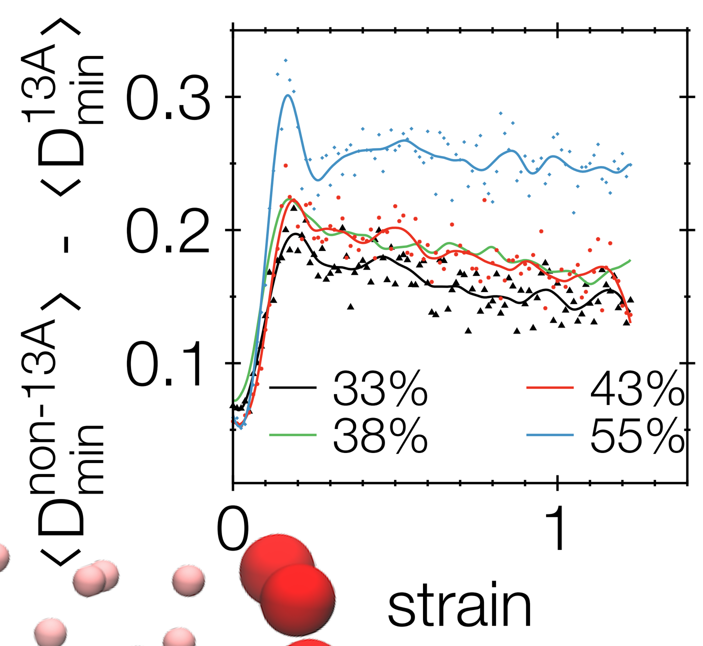


Fig. 6 Evolution of the **density of states** as a function of the applied strain. Saddles disappear as soon as the external shear is applied.

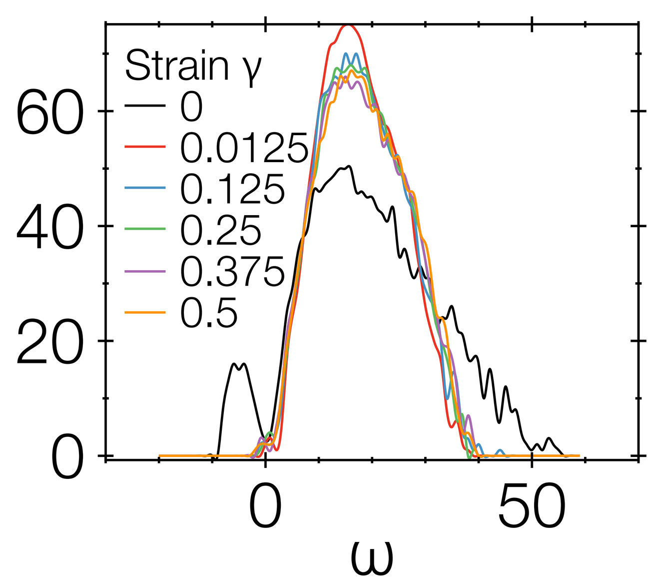
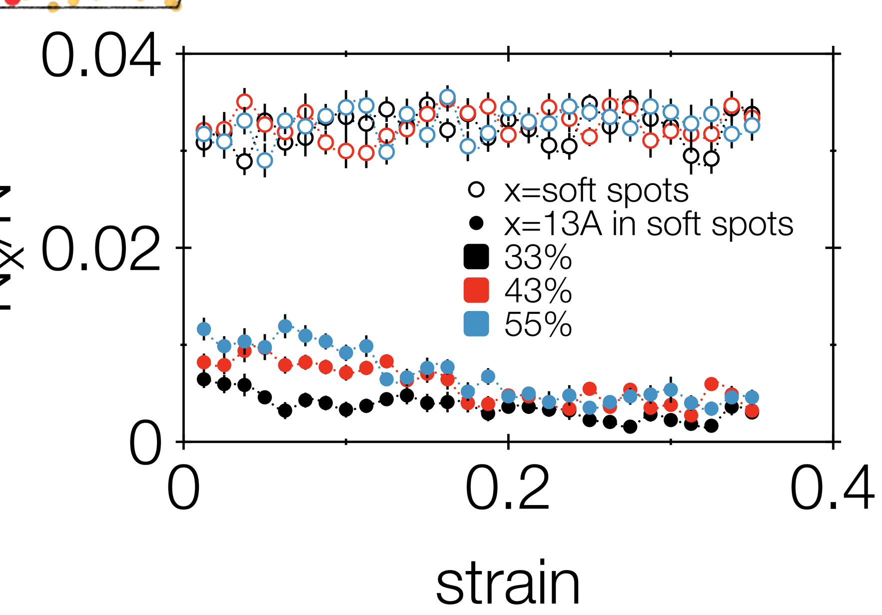


Fig. 7 The large majority of the soft spots is not localised into icosahedral regions, even when these occupy the most of the volume.



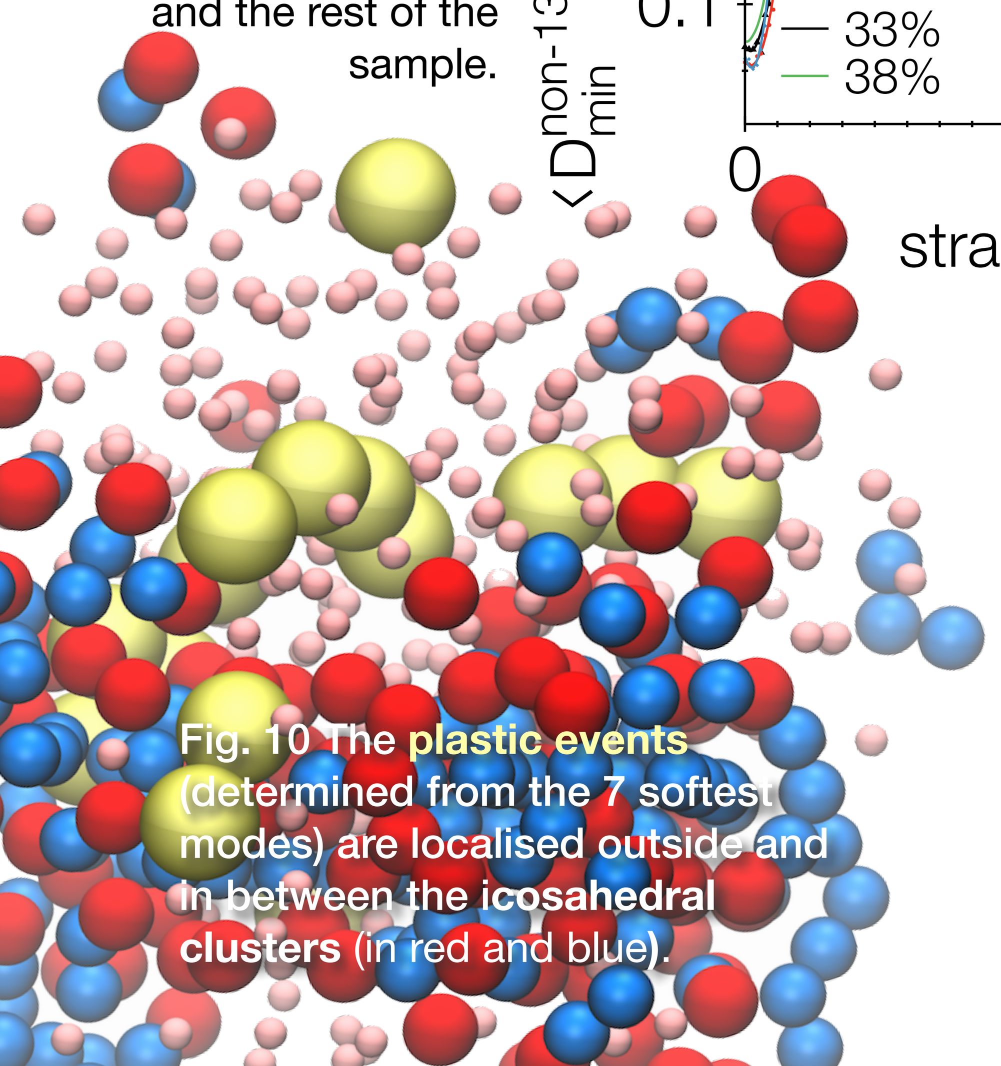


Fig. 10 The plastic events (determined from the 7 softest modes) are localised outside and in between the icosahedral clusters (in red and blue).

Conclusions. Using biased sampling techniques, we obtained **high concentrations** of LFS. These appear to be correlated with the **hardening** of the rheological response.
The **localisation** of the LFS is **anti-correlated** with non-affine **displacements** and mobility-triggering **soft-spots**, justifying the interpretation of the icosahedral LFS as the **backbone** of the solid structure of the considered glass former.

References & Acknowledgements

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