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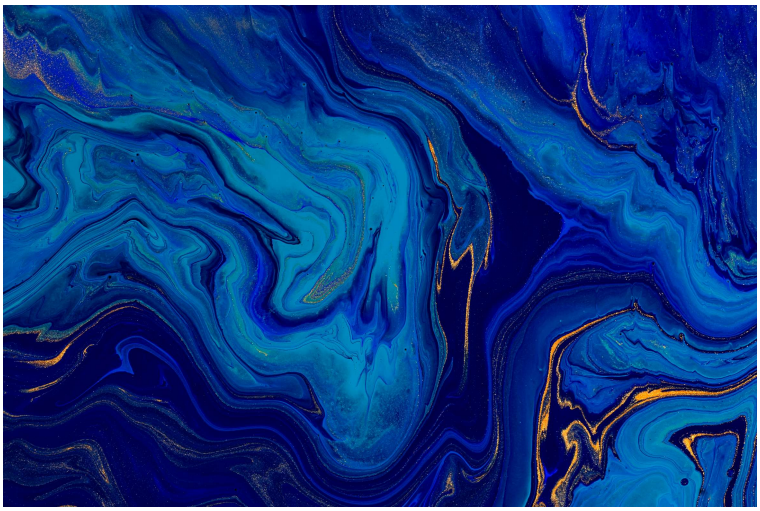
Slow and steady wins the race: a tale of molecules dancing in a different way



Macroscopic equilibrium phenomena require microscopic movement of molecules. Until now, the dynamics of liquids had been described considering a single type of movement known as structural relaxation. A Belgian research team from the ULB with the participation of dr. Cristian Rodríguez, lecturer in the Thermal Properties of Nanoscale Materials Group (GTNaM) at the UAB, have described a new movement, the SAP (Slow Arrhenius Process).

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A system is at equilibrium when its properties do not change with time. Experience tells us that such observation is, however, rarely encountered in nature. The transformation of buds into flowers and then fruits, the rearrangements of plates on the surface of planets, and even the whole human body over its lifetime are just a few, among the many, examples of systems far from equilibrium. With time, these systems struggle to reach equilibrium, meaning they rearrange and adapt to the environment to reach reduce their internal energy.

Since almost a century, we know that macroscopic phenomena of equilibration (e.g. an elastic rope that elongates upon traction, or an ice cube that melts when we bring it out of the freezer) require microscopic motion of molecules. By increasing the temperature molecules move faster, and equilibration is achieved within a shorter time. This fundamental principle reflects the beauty of physics and has powerful implications.

By observing how a material reacts to the application of small forces, we can follow the equilibration process and, hence, understand the trajectories of molecules, regardless how fast molecules move and how small are the distances they make.

Thanks to these experimental methods it was possible to observe that molecules of liquids need to cooperate to move around their positions. Molecular motion is achieved only upon a sort of collaborative action. The colder the temperature gets, the more the liquid becomes dense and viscous, and the more molecules need to coordinate their movements to equilibrate. For decades, the dynamics of liquids has been described by considering only this kind of motion, known as structural mobility.

Now, writing in Science Advances, an international team at the Laboratory of Polymer and Soft Matter Dynamics from the Université Libre de Bruxelles led by Prof Napolitano, with the participation of Dr. Cristian Rodríguez-Tinoco (currently, associate professor at UAB) has shown that molecules also know another way to move. They have identified a new molecular process, called SAP (slow Arrhenius process), that at high temperatures is slower than structural mobility and shows the characteristics of an “Arrhenius process”, that is, its rearrangements are not affected by density.

The experimental work of the ULB team replies to several unanswered questions of the dynamics of liquids. Laboratories all over the world had already observed that liquids can equilibrate in an efficient way which cannot be attributed to the structural process; the ULB team has verified that the molecules of different types of materials choose the SAP to reduce their internal energy. Importantly, following the route of the SAP is possible at any temperature: while the structural process becomes slower and slower upon cooling, at low temperatures, when the liquid is getting so viscous that it behaves almost as a solid, the new mechanism overtakes the old one. Thanks to its unique properties the SAP can ease the equilibration of materials within a reasonable time (days, months), at temperatures where the structural process would require geological (infinite) times.

The SAP can be pictured as a team of cyclists delivering food: they might be slower than cars during regular hours, but in the case of traffic jam, you can count on them to get a warm meal on your table.

Understanding the nature of the SAP has strong implications. In the design of new materials and their fabrication protocols, a better control of properties is achieved by identifying those conditions favoring mechanisms that do not depend on a change in the structure, as it is the case for the SAP. Moreover, as most raw and processed amorphous materials are stored in the low temperatures, the shelf time of these systems is significantly affected by potential equilibration through the new pathway discovered by the ULB team.

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References

Song, Zijian & Rodríguez-Tinoco, Cristian & Mathew, Allen & Napolitano, Simone. (2022). **Fast equilibration mechanisms in disordered materials mediated by slow liquid dynamics**. Science Advances. 8. 10.1126/sciadv.abm7154.

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