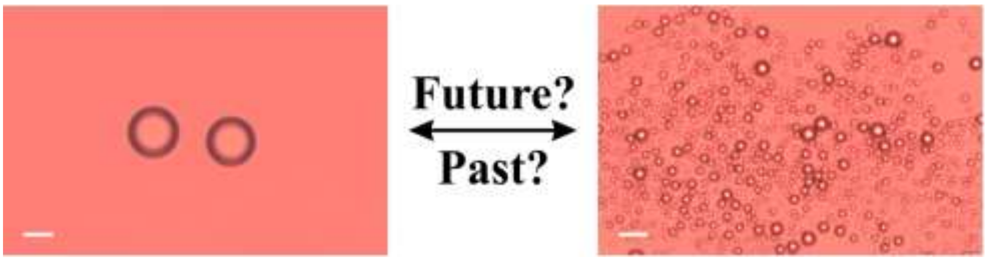
# The Emulsion Arrow of Time




It's not often one can stop the flow of time, let alone reverse it. Many creams promise to do this with dubious results. But in the case of emulsion experiments scientists at the University of Cambridge and University of Sofia have done just that with the physical processes that go on within the creams themselves.

Stoyan Smoukov, leader of the project explains: Emulsions are a curious state of matter with their own rules. When you break a glass, and it falls apart into thousands of pieces, you could never hope to put it back exactly as it was. This is so ingrained in our experience we can tell the flow of time by seeing the initial and final states of the glass. In emulsions the situation is similar, but time flows in the other direction: the tiny little pieces are the unstable state, and the whole glass (or in this case, single droplet) is the stable one. The broken-up liquid droplets have a self-healing tendency, and as emulsions age, many droplets coalesce and become few, or eventually one (backward arrow in the picture above).

Emulsions also make half the products we use every day – including consumer products (shampoos), foods (ice-cream, mayonnaise), drinks (Baileys), and cosmetics (creams, lotions). They are most commonly droplets of oil dispersed in water, with the help of soap-like (surfactant) molecules. Controling the size of the oil droplets is extremely important for the properties of the emulsions – the smooth taste of Baileys Irish cream and the gel-like consistency, texture and taste of mayonnaise.

Small droplets are often highly desirable. Lotions have been historically milky-white, due to scattering from micron-sized droplets, yet transparent lotions containing the same amount of oil are now possible since nano-sized droplets don't scatter the light. By doing work, one can break up large droplets again into little pieces, though some mechanisms for this are more efficient than others. The established industrial processes use mechanical shear to break up the droplets and require lots of work to do this, often 1000 times more than the extra surface energy stored in the newly created tiny droplet interfaces. This causes significant heating of the emulsions, and is the reason emulsions are not formulated to contain temperature-sensitive ingredients, such as proteins, and other biological ingredients, increasingly important in the pharmaceutical industry. "

As an alternative to mechanical breakup of droplets, several methods of "self-emulsification" have been developed which require large amount of surfactants and the introduction of a miscible chemical to change the stability of the large droplets. Even more recently, mixtures of surfactants at high concentrations have been found where a change in temperature can make the droplet interface temporarily unstable and cause droplet breakup. None of the processes so far take small fluctuations of temperature in the environment and cause droplet breakup.

By contrast, the team's process uses low surfactant concentrations (< 1% by weight), and achieves similar drop size decrease as in industrial high-pressure homogenization. With only a few degrees change in the surrounding temperature breakup is achieved not from outside forces, but from internal phase transitions occurring in the droplets (related to droplet shape changes we have reported before). This new process could be a breakthrough both in the industrial generation of emulsions in general, and specifically low-temperature pharmaceutical emulsion formulations, which have not been possible to achieve before on a commercial scale. We have just been awarded a translational Proof-Of-Concept grant by the European Research Council to create an industrially relevant prototype of the process. Some of the largest companies in Europe have expressed interest in it and would be partners in potential successful developments.

A broader, intriguing aspect of the work is the fundamental novel behavior of this simple system. Containing only 3 chemicals (water, soap (surfactant), and oil), it can still harness energy from a few degrees fluctuations around room temperature, which naturally occur in nature as well, and store them in the form of interfacial energy of the newly formed small droplets. Thermal fluctuations can effectively renew the small droplet, high energy state of the emulsion after it has decayed and self-healed to larger droplets. This is peculiar behavior for a non-living system and only exhibited by more complex non-equilibrium systems. The compositional simplicity, yet rich behavior of the system will allow insights into how non-living systems can harvest thermal energy from their environment and ratchet themselves up to higher-and-higher energy states. Similarly, the process overturns the simple picture of understanding the arrow of time in emulsions, if simple fluctuations of temperature can turn around its direction.

Stoyan Smoukov, Head, Active and Intelligent Materials Lab, Materials Science and Metallurgy,

University of Cambridge. Contact sks46@cam.ac.uk, 01223 334435