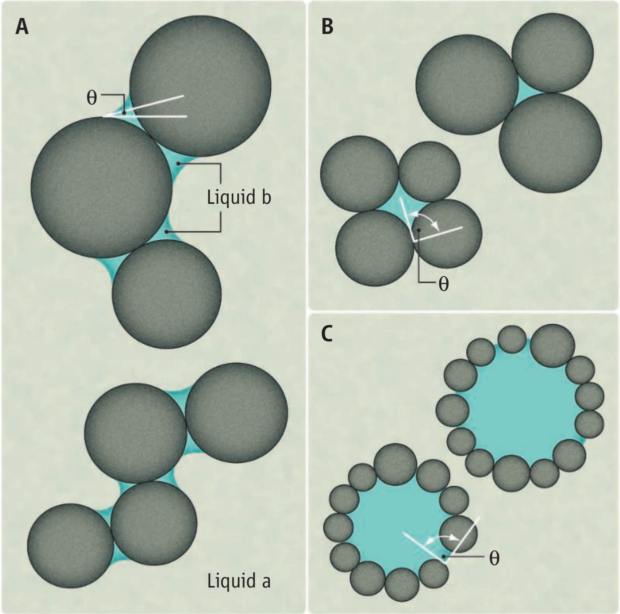
MATERIALS SCIENCE

Controlling the Flow of Suspensions

Adding a small amount of an immiscible liquid to a suspension can change it from a viscous fluid to an elastic gel.

Hans-Jürgen Butt

If you've painted a wall, you know that you want the paint to flow smoothly onto the surface but be viscous enough that it doesn't drip. Paint is a suspension—small, solid particles of pigment and polymer dispersed in a liquid—and manufacturers devote much effort to controlling its flow behavior, or rheology. Suspension rheology is critical not only in coatings but also in many food and materials processing steps, and it depends on two factors. First, the content and shape of the dispersed particles are important, but these factors usually cannot be varied to optimize performance. The size and shape of the particles are usually predetermined, and a high volume ratio of particles to solvent is often required. The second factor is the interaction between the particles, which affects viscosity. To achieve low viscosity yet deliver a high volume ratio of particles, the particles should repel each other. To achieve a high viscosity and create an elastic material like a gel, the particles need to aggregate via attractive forces. Forces between the particles are determined by their surface properties and are traditionally adjusted by adding surfactants. On page 897 of this issue, Koos and Willenbacher (*1*) propose another option, the addition of a small amount of a second liquid, immiscible with the primary liquid.



θ <<90°, wetting

θ ≥ 90°, nonwetting

Stabilizing dispersed phases. These schematic representations show how suspensions and emulsions can be stabilized with a third added phase. **(A)** Dispersed particles forming a pendular state in a primary liquid a (continuous phase, gray). The particles are kept together by pendular menisci of a second, immiscible liquid b (blue). This happens if the contact angle is low and the added liquid wets the particles. **(B)** Koos and Willenbacher report on a capillary state, in which drops of the secondary liquid form the center of particle agglomerates. In this case, the contact angle is about 90° and the added liquid fails to wet the particles. **(C)** A similar effect is used to stabilize Pickering emulsions, where colloidal particles prevent droplets in an emulsion from merging into larger droplets.

Koos and Willenbacher first dispersed hydrophilic glass beads in a primary liquid (an organic solvent, diisononyl phthalate) and then added 1 weight percent of water as a secondary liquid. Upon stirring, the suspension changed from a viscous fluid to an elastic or gel-like material. Such a transition from a viscous to an elastic state caused by trace amounts of a secondary liquid had already been observed (*2*, *3*) for the case in which the added liquid wets the particles. A pendular water meniscus forms around the contact point between two particles. Once such a meniscus has formed, interfacial tension draws the particles together. These capillary forces (*4*–*6*) are relatively strong, much stronger than the van der Waals forces. The particles aggregate (*7*) and form an elastic network (see the figure, panel A).

Capillary forces act between two particles if the liquid-liquid interface of the pendular meniscus forms a low contact angle θ with the solid-liquid interface. On a flat surface, the secondary liquid would spread and from a flat pancake. However, capillary forces should not be operating for high contact angles. Therefore, Koos and Willenbacher were quite surprised to observe a similar transition when repeating the experiment with hydrophobized glass beads. Hydrophobized glass beads form a large contact angle with water in nonpolar liquids. Koos and Willenbacher explained this surprising result in terms of a collective effect in which several particles gather around a droplet of water and protect it from forming a large interfacial area with the bulk, nonpolar liquid (see the figure, panel B). Here, the contact angles are around or above 90°, and the fluid would tend to form droplets on the surface. In contrast to the pendular state, this is called the capillary state (*1*, *3*). Koos and Willenbacher studied many different combinations of immiscible liquids and solid particles and observed the same changes in the rheological properties, which suggests that this effect could be seen in many other suspensions.

A closely related effect has been used for more than a century to stabilize emulsions (a mixture of one liquid dispersed in a second immiscible liquid, such as oil in water). A Pickering emulsion is stabilized by adding colloidal particles that move to the oil-water interface (*8*, *9*) and prevent drops of the secondary liquid from merging (see the figure, panel C). In contrast to the capillary state in suspensions, the amount of secondary liquid in a Pickering emulsion is comparable to that of the primary liquid, and the drops are much larger than the particles. More recently, colloidosomes (*10*, *11*), which have potential applications in drug delivery, and small clusters of a defined number of particles—also called colloidal molecules (*12*, *13*)—have been made by confining particles to the interface of oil drops in water, or vice versa.

What determines whether a suspension enters the pendular state or the capillary state? The answer lies in Young's equation, which relates the interfacial tensions to the contact angle: $\cos\theta = (\gamma_{SA} - \gamma_{SB})/\gamma_{AB}$. Here, γ_{SA} is the interfacial tension of the solid particle with the primary liquid A, γ_{SB} is the interfacial tension of the solid particle with the secondary liquid B, and γ_{AB} is the interfacial tension of the liquid-liquid interface. If the secondary liquid wets the particles better than the primary liquid ($\gamma_{SA} > \gamma_{SB}$), the contact angle is low and the pendular state should form. If the secondary liquid wets the particle surface less or equally well ($\gamma_{SA} \leq \gamma_{SB}$), the contact angle is ≈90° and the capillary state should form.

The discovery of Koos and Willenbacher will have considerable impact. Process engi-

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neers now have an additional way of tuning the flow properties of suspensions in a simple, environmentally friendly, and inexpensive manner. Rather than adding surfactants or polymers, a suitable secondary liquid can be added. The discovery is also a warning to avoid contaminating a suspension with an immiscible secondary liquid and risk a drastic increase in suspension viscosity (clogged pipes or jammed machinery).

For basic research, their findings lead to several questions. What is the influence of added surfactants and polymers, considering their adsorption to all three interfaces? What is the influence of polydispersity, particle shape, or surface roughness? As in the case of granular materials (*14*, *15*), the interaction energies between particles are much higher than the thermal energy that governs particle and solvent motions. Large energy barriers have to be overcome in a transition, so a system is likely not to be in thermodynamic equilibrium. This situation makes a systematic study more difficult because the structure and properties of a suspension will depend on its history.

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NEUROSCIENCE

Creating Stable Memories

J. David Sweatt

Epigenetic mechanisms are involved in "tagging" rat neurons active in long-term memory of food odors.

Social animals with a keen sense of smell, such as rats, can teach each other about the safety of new foods by a practice called social transmission of food preference (STFP). In this olfactory learning paradigm, a rat that has just eaten can familiarize another rat with the taste odor of a new food by allowing the naïve rat to sniff its breath. The naïve rat apparently infers that the novel food is safe to eat because another rat has eaten it, and exhibits greatly diminished fear of the new food at first exposure. On page 924 of this issue, Lesburguéres *et al.* (*1*) describe their discovery of two fascinating aspects of this form of long-term memory: Specific neurons or synapses in the cerebral cortex are specifically "tagged" and thereby allocated to participate in a memory for a particular food odor, and this process involves epigenetic molecular mechanisms.

STFP is a form of associative memory that depends on a particular part of the brain, the hippocampus (HPC), and can last an animal's lifetime (*2*–*4*). When being formed, the memory is downloaded from the HPC to the cortex via a process called systems consolidation, a term that describes an ongoing synaptic dialog between the HPC and the orbitofrontal cortex (OFC) that occurs over the course of about 1 week (*5*, *6*). In their experimental paradigm, Lesburguéres *et al.* showed that STFP is dependent on the OFC at 30 days after the training experience ("remote" memory), but independent of the OFC at 24 hours ("recent" memory). Thus, STFP is HPC-dependent for its acquisition, and the long-term storage of the olfactory information requires the OFC.

Lesburguéres *et al.* investigated how the interplay of neural circuits in the HPC and OFC allows systems-based consolidation. In their experiments (see the figure), they found that the glutamate receptor antagonist CNQX blocks memory when infused into the OFC during the 2 weeks immediately after a rat is exposed to the novel taste. The observation of memory loss with blockade of OFC activity immediately after novel taste odor exposure raised a conundrum. At 30 days, taste odor memory is consolidated and stored in the OFC. Hence, during the first week that the memory is being processed in the HPC, it does not yet reside in the OFC. So how can early inhibition of the OFC block its subse-

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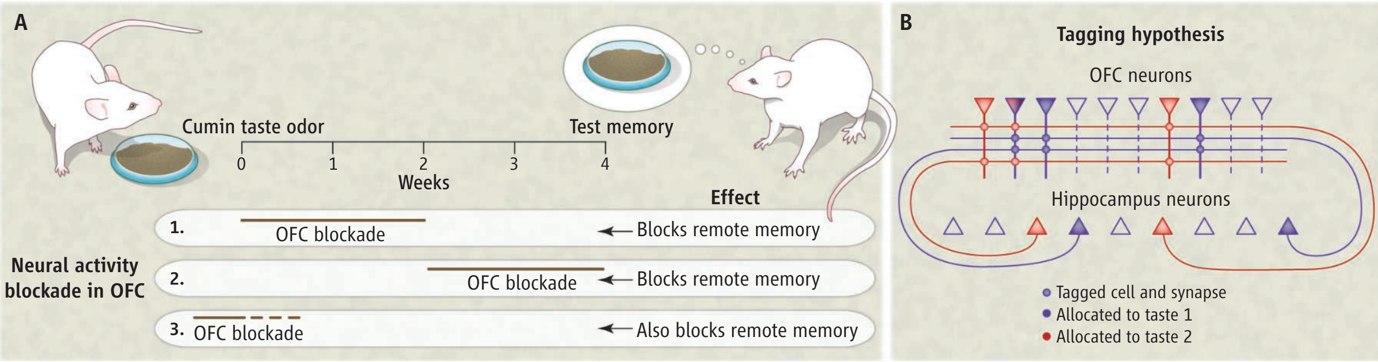

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Taste test. (**A**) Infusing CNQX into the OFC blocks neuronal firing and leads to loss of long-term memory consolidation, both when infused early (during the 2 weeks immediately after novel taste exposure) and late (in weeks 3 and 4). (**B**) After exposure to a novel taste, a subset of OFC neurons are "tagged" for different taste memories, marking them for subsequent activity-dependent plasticity driven by the hippocampus. This tag might reside at the synaptic or at the whole-cell level (*15*).

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Editor's Summary