cial applications wherever the value of the solute is high, its concentration in the matrix is low, and conventional solvents lead to either recovery problems or difficulties with regulatory agencies. This work successfully brings to an end a decade-long and often maddening search for materials that will form reverse micelles in CO_2 and will hopefully inspire others to enlarge the catalog of CO_2 -soluble ampiphiles in the future.

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"Negative Viscosity" in a **Magnetic Fluid**

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Ultrastable magnetic fluids (MFs) attract scientific and technological interest because they remain liquid when highly magnetized, even in the most intense applied magnetic fields. The fluids are distinguished from ordinary fluids by the body and surface forces that arise, yielding new fluid mechanical phenomena (1). Ordinarily MFs exhibit the Newtonian rheology of water and other common liquids, with stress proportional to rate of strain, albeit the coefficient of viscosity increases in applied magnetic field. This behavior was believed to be general, but recent theoretical analysis predicts (2) and experimental investigation

demonstrates (3) that under appropriate conditions with a time-varying field, the viscosity of MF exhibits a substantial reduction, that is, a negative viscosity component. The effect is attributable to the generation of asymmetric stress in MF; a corroborating analysis with generalization to elliptically polarized fields is given by Zahn and Greer (4). Mere generalization of the Navier-Stokes equations in which equilibrium body and surface forces of magnetic



Fig. 1. Magnetic fluid in a colloidal dispersion of single-domain magnetic particles of about 10 nanometers. The sketch illustrates particles stabilized with a molecular coating; alternatively, the particles may be charge stabilized

origin are introduced is quite successful in predicting the response of MF to steady magnetic fields but cannot account for the new phenomenon (5, 6).

Magnetic fluids are colloidal solutions of magnetic nanoparticles suspended in a fluid carrier (Fig. 1). Each particle is a permanent magnetic dipole, and when the particle is not too small, the orientation of the dipole is locked into the crystal axis of the particle. A repulsive force acts as an elastic cushion, preventing the particles from sticking to each other. Thanks to Brownian translational motion, the particles do not settle in gravitational or magnetic

fields. By the same token, Brownian rotational motions prevent complete alignment of the dipoles with applied fields. Thus, when the field has a changing direction or magnitude, the magnetization is unable to track the field closely and becomes unequilibrated. This lag process is responsible for the negative viscosity effects.

The earliest observation of an unequilibrated response in MF was reported in 1967 (7). A rotating magnetic field applied to MF in a beaker spun the fluid into motion. Soon, another investigator repeated the experiment, placing the beaker on a rotating turntable. Surprisingly, the fluid rotated the "wrong way," that is, the beaker

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rotated in the direction of the field while the fluid rotated in the opposite direction. For a long time, the mechanism responsible for this behavior was not understood. A magnetic field exerts an orienting influence on each suspended magnetic particle, similar to the effect on a compass needle, and when the particles are spun relative to the carrier fluid, a dissipative viscous coupling results. P. G. deGennes noted from the consideration of symmetry that no velocity field can be generated if the spin field is spatially uniform (8). Zaitsev and Shliomis (9) contributed analysis imposing a condition of retarded spin at the wall and, through diffusion, a nonuniform distribution of spin in space. Gradients of the spin produce a calculable body force from which the spin-up motion of the fluid ensues. However, the observed flow speed is orders of magnitude larger than predicted. Moreover, the predicted direction of the flow is opposite that of the observed behavior. As it turns out, the problem is not with the theoretical framework, which introduces an equation of angular momentum balance (10) and a relation for magnetic relaxation, but with the assumptions made in applying the equation set.

Thus, subsequent theories invoked spatial nonuniformity of the applied field, presence of temperature gradients, and onset of flow instability to reconcile theory with experiment. Finally in 1989, experiments and a new reading of the known relation for magnetic stress (11) showed that the direction of fluid rotation in relation to the field's rotation depends on the curvature of the free surface meniscus, whereas a flat meniscus yields no coupling. Thus, the spin-up phenomenon is a surface not a volume effect.

A striking visual display of the asymmetric stress is exhibited by drops of MF (12) suspended in another fluid. The drops are produced as a phase-separation product possessing a low value of interfacial tension. Subjected to a rotating magnetic field, the drops first elongate and spin and then develop spiny arms reminiscent of starfish. Depending on experimental conditions of frequency and field intensity, the number of arms undergoes transitions and other dynamics are observed, such as an eel-like form that curls around and attaches to its own flank. The questions these flows raise could keep theorists occupied for years.

For study of the negative viscosity phenomenon, a Poiseuille flow is established in a horizontal capillary tube 1 mm in diameter. A pressure gradient is formed by the difference in MF level between the inlet and outlet of the tube. The tube is put inside a solenoid that provides an alternating magnetic field at frequencies up to 1 kHz with magnetic intensity up to 0.2 T parallel to the flow direction. A MF having viscosity of

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Fig. 2. Experimental reduced viscosity. $\eta_{t}(B, t) = [\eta(B, t) - \eta(B, t)]$ $\eta(0, 0)]/\eta(0, 0)$ versus magnetic field B for different frequencies f

 $0.077 \text{ N} \text{ s} \text{ m}^{-2}$ in the absence of field and a viscosity increase to 0.220 N s m⁻² in a field of 0.2 T experiences a viscosity reduction to 0.100 N s m⁻² at 50 Hz, 0.077 N s m⁻² at 250 Hz, and 0.058 N s m⁻² at 700 Hz (Fig. 2).

The alternating, linearly polarized field induces rotational swings of the particles but does not single out any preferred direction of their rotation. Therefore, an averaging over a physically small element of volume results in a spin of zero. Any flow with a vorticity not zero is sufficient to break the degeneracy of the rotation direction and leads to a nonzero macroscopic spin rate of the particles. This transforms a part of the alternating field energy into kinetic energy of the fluid that manifests itself in a reduction of the total viscosity.

Earlier work (13) treating asymmetric stress when the product of frequency and relaxation time is less than unity and utilizing a Debye-like relaxation relation predicts viscosity increases in steady applied field that match well with experiment (14). A more rigorous magnetization equation derived from a Fokker-Planck equation yields improved predictions when the product exceeds unity.

In a recent study of oscillating field applied to a rotating cylinder of glycerinebased MF, a resonance of the off-axis component of magnetization gives a rather direct and vivid indication of the negative viscosity effect (15).

There are applications of MF in areas ranging from tribology to instrumentation to medicine. Virtually every personal computer's hard drive contains MF rotaryshaft seals that prevent contaminants from entering. The seals also are widely used in vacuum to air feedthroughs in the manufacture of single-crystal silicon and subsequent fabrication into integrated circuits. Drive coils in millions of audio speakers are cooled to prevent self-destruction by MF held in place with permanent magnets. Other applications in stages of development include the precision machining of

ceramics, high-speed printing, sink-float separation of minerals, inclinometers for directional drilling in oil fields, and means for enhancing signals in medical magnetic resonance imaging (MRI) scans. It is too early to say what new applications, such as tunable dampers, the discovery of negative viscosity may make possible, or whether the phenomenon will remain a laboratory curiosity. Intriguing is the possibility that if the viscosity is driven to zero, spontaneous patterns of flow may develop. In another direction, an interesting anal-

gravitational dipoles that likewise obey asymmetric stress relations (16).

ogy exists with suspensions of

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Ion Channels: Opening the Gate

Much of neuronal action is driven by sodium and potassium ion channels. These cell-membrane proteins respond to voltage changes by opening and letting ions through when the normally negative interior of the cell becomes more positive. The S4 region of the protein, with its charged residues, is thought to sense this voltage change and shift its position in response (1), thereby mediating the tiny movement of charge that can be measured as the channel prepares to open—the gating current (2).

Because we know little about the three-dimensional structure of ion channels (no crystal structure exists for any eukarvotic channel), our occasional glimpses of how this really happens have been frustratingly indirect. Now two key studies (3, 4) offer a clearer picture of S4 movement in the channel during gating and ameliorate our frustration at not having the crystal structure of an ion channel, at least temporarily.

Yang and co-workers report in the January issue of Neuron (3) that, for the sodium channel, the S4 region moves a considerable amount of charge across the protein in response to a voltage change. Their trick is to probe the accessibility of introduced cysteine residues to cysteine-modifying agents, revealing that two of the charged residues in S4 and presumably the hydrophobic residues between them move from a position that is accessible from the inside of the cell to one that is accessible from the outside. This large movement

of charge completely across the hydrophobic membrane is possible because the charges seem to move through a very short "hole" that contains at most one charged residue of S4 at a time. In a complementary report in Science (4) Mannuzzu et al. describe their success in engineering a fluorophore into the S4 region of the potassium channel; by continually monitoring its accessibility to the extracellular medium, they have been able to follow the movement of these residues of S4 in real time. They find that at least seven S4 amino acids move from a buried position into the extracellular space simultaneously with the gating current. This same group has also shown that potassium channel S4 moves across most of the transmembrane core during gating (5).

The identity of S4 as the voltage sensor of these ion channels is more secure now that we have "seen" it move in response to voltage changes in a way consistent with the job of carrying the gating current. Future studies will tell us whether other parts of the protein also contribute and hopefully elucidate the basis of the exquisite voltage sensitivity of these proteins.

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