plantations of sitka pine or other exotic tree species. But successful management of the grouse-shooting industry — the 'Glorious Twelfth' of August, which marks the start of the shooting season, and all that — depends on high population densities of grouse. So the hen harrier's depredations are understandably viewed with disfavour by moorland managers. Although hen harriers and their nests have received full legal protection since 1954, there are abundant anecdotal reports of their persecution.

Etheridge and colleagues[3] have carried out a thorough study of the breeding productivity, natal dispersal and survival of hen harriers over the eight-year span 1988–95. The study covered moorland managed for grouse shooting, other heather moorland and young conifer forests in the Scottish uplands. The authors found 'nest success' much lower on grouse moors than elsewhere: 0.8 fledglings per breeding female per year, compared with 2.4 on other moorland and 1.4 in young conifer forests. Human interference with nest sites was documented on half of the grouse moor estates, accounting for at least 30% of breeding failures there. Moreover, annual survival of female hen harriers breeding on grouse moors was around half that on other moorlands, the cause being killing of the birds by humans. On average, 55–74 breeding females were killed each year over the eight-year study, representing 10–15% of the total population of breeding females in Britain (excluding Orkney).

Etheridge *et al.* further show that these losses on grouse moors would be unsustainable, leading to the rapid disappearance of hen harriers, were it not for breeding in the other habitats. Natal dispersal distances for both male and female hen harriers exceed 10 km, and harriers fledged from one kind of habitat were commonly found breeding in another. In short, moorland managed for grouse shooting is currently acting as a sink, with about 70% of its female recruits coming from other moorland or from conifer forests.

Overall, Etheridge *et al.* calculate that the total population of breeding female hen harriers in Britain is likely to be slowly falling. Their estimate is a decline of around 6% per year, but the many uncertainties are such that this is not significantly different from a zero rate of decline, or even a very small increase; conversely, the situation could be worse than estimated. We need a repeat of the Royal Society for the Protection of Birds' 1993 nationwide survey of hen harriers[2]. But at the least Etheridge and colleagues' study suggests that, without the current persecution on grouse moors, Scotland's population of hen harriers would begin to increase at something like 13% a year.

From the gamekeepers' viewpoint, the indications are that grouse breeding success and survival would be higher in the absence of hen harriers and other raptors[5,6] (mainly peregrine falcons but to a small extent short-eared owls and golden eagles). So their persecution on grouse moors is not unreasonable (although it is against the law). We have a real problem here, with conservation interests on both sides: the grouse-shooting industry helps to conserve traditional British uplands and their vegetation, which would otherwise be likely to disappear under pine plantations; but the economic viability of this industry is seen by some of its practitioners to require the illegal killing and harassment of birds of prey. Underlying this dilemma, Etheridge *et al.*[3] observe that "the sport shooting of red grouse and other game birds may not continue to be acceptable to the general public if its proponents argue that it can be sustained only by the persecution of rare birds of prey". The existence of an increasingly influential lobby against blood sports in general adds force to this argument.

So what else can be done? Phillips and Watson[7], and others, have suggested that more active management of heather moorland, with optimal schedules of burning to promote heather as food and cover for red grouse, could help. Although desirable, this approach would be expensive for a grouse-shooting industry that is arguably at the margins of profitability. Perhaps a more realistic way of reconciling the industry's interests with raptor conservation is to lay off the hen harriers and to concentrate more on the (legal) control of the relatively abundant crow and mammal predators of red grouse, particularly red foxes, whose "populations and distributions are less sensitive to culling than those of the hen harrier"[3]. □

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1. Newton, I. *Population Ecology of Raptors* (T. & A. D. Poyser, Berkhamsted, Herts, 1979).
2. Bibby, C. J. & Etheridge, B. *Bird Study* **40,** 1–11 (1993).
3. Etheridge, B., Summers, R. W. & Green, R. E. *J. Appl. Ecol.* **34,** 1081–1105 (1997).
4. Krebs, J. R. & May, R. M. *Nature* **343,** 310–311 (1990).
5. Redpath, S. M. *J. Appl. Ecol.* **28,** 659–671 (1991).
6. Hudson, P. J. *Grouse in Space and Time* (The Game Conservancy, Fordingbridge, Hants, 1992).
7. Phillips, J. & Watson, A. in *Heaths and Moorland: Cultural Landscapes* (eds Thompson, D. B. A., Hester, A. J. & Usher, M. B.) 344–361 (HMSO, Edinburgh, 1996).

Fluid dynamics

All stressed out

Mark Robbins

On page 360 of this issue[1], Peter Thompson and Sandra Troian report the discovery of remarkable behaviour at the interface between fluids and solids. They use a computer model to follow the motion of individual atoms in a fluid flowing over a solid surface. As the fluid is forced to flow more quickly, it suddenly begins to slip more easily over the solid. Even more surprisingly, the increase in ease of slipping follows a universal law. This transition in behaviour could affect macroscopic flow patterns in spreading, extrusion and other important industrial processes.

Scientists and engineers usually model fluid flow using continuum theories. Rather than following the motion of each atom, they describe the fluid by a few continuous variables that specify the average properties of atoms in each small region of space. These variables are the mean velocity, density and pressure. The Navier–Stokes equation relates these variables, and can be solved to see how they change with time.

The continuum approach works well if changes occur over lengths much greater than interatomic distances. It runs into trouble at the sharp interface between a fluid and a solid, where the type of atom changes abruptly. So such interfaces must be included as boundary conditions on the continuum equations. Historically, these boundary conditions were guessed at and then tested by solving the equations and comparing the solutions with experiments. But tremendous advances in computing power now make it possible to test these boundary conditions with much greater precision and resolution than macroscopic experiments can[2].

Mechanical equilibrium imposes two simple constraints on interfaces in any steady, time-independent fluid flow: both the pressure perpendicular to the interface and the shear stress tangential to the interface must be the same on the two sides, or else the interface will accelerate. The remaining boundary condition is some relationship between the velocities on the two sides of the

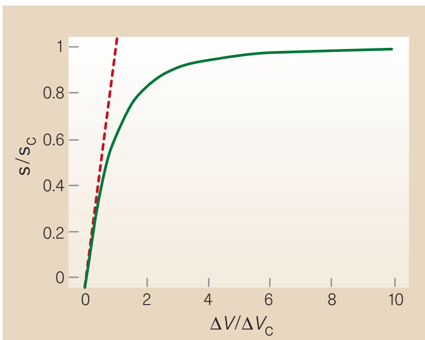

Figure 1 **An apparently universal relationship between shear stress σ and the slip velocity ΔV between fluids and solids. The shear stress saturates at a value σ_c as the slip velocity diverges. ΔV is the slip velocity that would be observed at σ_c if the relationship were linear (dotted line).**

interface. The usual, 'no-slip' boundary condition is an assumption that the velocities are the same (that is, fluid atoms don't slip over an adjacent solid).

This assumption describes most macroscopic flow patterns very well. The best-known exceptions are cases where a sharp corner forces the velocity to change rapidly, such as in the spreading of a fluid over a solid. The no-slip boundary condition would require the velocity within the fluid to change infinitely fast near the corner where the fluid interface intersects the solid, making it infinitely hard to spread butter or to get water to flow along a glass into your mouth. Fortunately, the no-slip boundary condition breaks down at molecular scales. In the past decade, molecular dynamics simulations[3,4] have shown that large stresses can cause slip at the corner, and the flow here cannot be described by the Navier–Stokes equation.

Now Thompson and Troian have discovered a way for the no-slip rule to break down on macroscopic scales. They consider a fluid between two parallel plates. The bottom plate is stationary, and the top plate slides over it with velocity U at a fixed height h. If there is no slip, the velocity in the fluid goes continuously from zero (the velocity of the bottom wall) to U as the height increases from zero to h. The shear rate $\dot{\gamma}$ in the fluid, defined as the derivative of the velocity with respect to height, is then U/h. Any slip can be characterized by a length L_s which is the apparent increase in thickness of the fluid at each wall that would be needed to reconcile the velocity difference with the actual shear rate, $\dot{\gamma} = U/(h+2L_s)$.

Previous simulations have found many cases where the no-slip condition breaks down[2,5], but the slip length is usually only a few atomic diameters. This means that slip only becomes relevant in atomically thin films, where h is comparable to L_s. Thompson and Troian find similar results at low shear rates. However, as the shear rate increases towards a critical value $\dot{\gamma}_c$, they find a sharp divergence of L_s that follows a universal law. This means that L_s becomes comparable to the dimensions of ordinary pipes or nozzles, and would need to be included in models of fluid processing. One useful consequence should be a saturation in the friction of thin lubricating films.

Because $\dot{\gamma}_c$ has units of inverse time, it would be natural for it to reflect a characteristic timescale of atomic motion, such as the time taken for a fluid atom to respond to forces exerted by the solid. However, this is not born out by the simulations. Perhaps the transition is instead controlled by the shear stress σ. Within the fluids studied by Thompson and Troian, this is proportional to the shear rate. However, the stress is more directly associated with the interface, having the same value there as in the fluid, whereas the shear rate is only a property of the bulk fluid. The divergence of L_s at $\dot{\gamma}_c$ implies that the velocity difference ΔV between the first layer of fluid and the solid diverges at $\sigma_c = \mu\dot{\gamma}_c$, where μ is the viscosity of the fluid. Equivalently, the maximum stress that the fluid–solid interface can sustain is σ_c. Figure 1 shows the functional relationship between σ and ΔV that is implied by Thompson and Troian's universal slip law.

The stress applied by the solid walls on adjacent fluid atoms comes from the variation of the potential energy of their interaction φ. Thompson and Troian find that $\dot{\gamma}_c$, and thus σ_c, scales as a power of a 'roughness parameter' that is a function of the gradient of φ. This is consistent with the idea that the transition is controlled by the shear stress. It will be interesting to see how surface roughness and other features of real surfaces affect Thompson and Troian's transition. □

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1. Thompson, P. A. & Troian, S. M. *Nature* **389,** 360–362 (1997).
2. Koplik, J. & Banavar, J. R. *Annu. Rev. Fluid Mech.* **27,** 257–292 (1995).
3. Koplik, J., Banavar, J. R. & Willemsen, J. F. *Phys. Rev. Lett.* **60,** 1282–1285 (1988).
4. Thompson, P. A. & Robbins, M. O. *Phys. Lett.* **63,** 766–769 (1989); *Phys. World* **3,** No. 11, 35 (1990).
5. Thompson, P. A. & Robbins, M. O. *Phys. Rev. A* **41,** 6830 (1990).

Solvents

Molecular trees for green chemistry

Joan F. Brennecke

Because carbon dioxide is nontoxic, nonflammable, abundant and cheap, it ought to be every scientist's and engineer's favourite solvent for extractions, separations and reactions. Unfortunately, even at dense liquid or supercritical conditions, its ability to dissolve polymeric, ionic or highly polar species is exceedingly limited. On page 368 of this issue[1], Cooper *et al.* show how a fluorinated dendrimer can be used to extract strongly hydrophilic compounds from water into liquid CO_2, considerably expanding the applicability of CO_2 as a solvent.

CO_2 and 'green chemistry' have become inextricably intertwined in recent years (the latest example being the "1997 Green Chemistry and Engineering Conference" held in Washington DC on 23–25 June 1997). This may seem ironic in light of the bad press it has endured in connection with global warming, but using CO_2 as a solvent does not result in any net production. In fact, most CO_2-based processes are designed to recycle and reuse essentially all of the CO_2. With this in mind, the excitement about CO_2 has developed because of its potential to replace hazardous organic solvents, especially chlorinated liquids and freons. When leaked into the atmosphere these compounds contribute to stratospheric ozone depletion, and the worst of them, the chlorofluorocarbons, have already been banned. In addition, many of the chlorinated solvents are carcinogens or suspected carcinogens, posing a health risk to chemical-plant workers, and to the general public if substantial leaks or spills occur.

CO_2 has other attractive features beyond its possible use as a substitute for less palatable organic solvents. Above its critical point (31 °C and 73.8 atmospheres), where the distinction between a liquid and a gas disappears, the density of CO_2 can be varied by almost an order of magnitude with relatively small changes in temperature or pressure — so its solvating power can be tuned and controlled. This should allow easy downstream separation: whether the dissolved species is a small organic molecule or a macromolecular assembly such as a micelle or a dendritic polymer, it can probably be enticed to separate from the CO_2-rich phase by appropriate adjustment of the solution density.

Supercritical fluids can also allow single-phase reactions, avoiding the limits imposed by mass transfer between two phases. In other reactions, rates and selectivities are better than can be achieved in liquids[2,3]. Some of these attractive features have long been used commercially in the extraction of

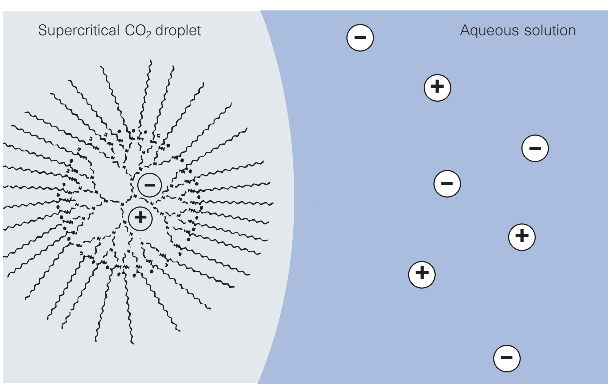

Figure 1 **A dendrimer in a droplet of carbon dioxide. These highly branched polymeric surfactants have fluorinated tails, which make them soluble in non-polar CO_2, and they are able to pull into solution polar and ionic species that are normally insoluble in CO_2. This should help supercritical CO_2 replace environmentally damaging conventional solvents.**