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
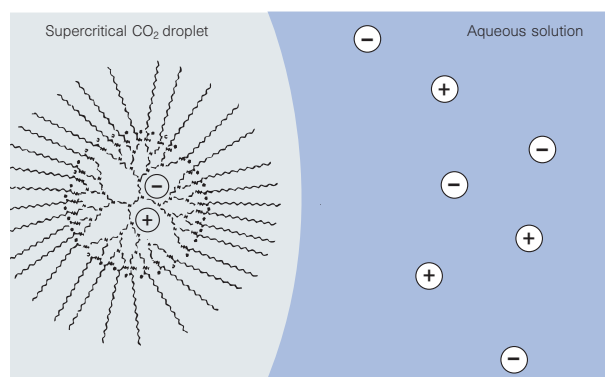

Figure 1 **A dendrimer in a droplet of carbon dioxide. These highly branched polymeric surfactants have fluorinated tails, which make them soluble in non-polar CO_2, and they are able to pull into solution polar and ionic species that are normally insoluble in CO_2. This should help supercritical CO_2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

small, relatively nonpolar compounds[4] (for example, the decaffeination of coffee and tea, and the extraction of flavours and aromas from natural products such as hops) and in the separation of similar compounds using supercritical-fluid chromatography. The two major drawbacks of supercritical CO_2, or liquid CO_2 at near-ambient temperatures, are the need for high pressures (approximately 50–350 atmospheres) and its difficulty in dissolving polymeric, ionic or highly polar species.

Whereas the requirement of high pressure is unavoidable, there have been a number of clever partial solutions to the limited-solubility challenge. An early idea was to add small amounts (1–5 mol%) of a co-solvent to the CO_2, generally intermediate in size and polarity between CO_2 and the target solute. This approach has been extremely successful and can increase the solubility of heavy organic solutes in CO_2 by an order of magnitude or more, especially where some specific chemical interaction such as hydrogen bonding occurs between the co-solvent and the solute.

This idea can be extended to extract metals into CO_2 by the addition of chelating agents. Conventional chelating agents such as acetylacetone and dithizones are effective, and their perfluorinated versions, as well as custom-made perfluoroether and silicone-based polymeric chelating agents, provide even greater solubilities of metals[5].

For reactions that require both hydrophilic and hydrophobic constituents, one successful[3,6] solution is the use of phase-transfer catalysis. But more recently, strategies for making hydrophilic compounds soluble have concentrated on forming organized molecular assemblies. A great success has been the identification of CO_2-loving perfluoropolyether surfactants, which in CO_2 form reverse micelles — hollow spheres of molecules with their hydrophilic heads on the inside. Their water-filled cores are capable of solubilizing proteins[7] and supporting ionic chemistry[8].

Now, in the work of Cooper et al.[1] we have an example of how a fluorinated dendritic polymer can be used in a similar way to further extend the applicability of CO_2 (Fig. 1). Dendrimers are highly branched polymers that form roughly spherical shapes in solution, acting like a micelle made out of a single surfactant molecule. Because the dendrimers used by Cooper and colleagues are fluorinated, they are soluble in CO_2, which is nonpolar. But the interior sections of the dendrimers are polar, and can trap highly polar or even ionic guest molecules. Thus the dissolved dendrimers make CO_2 a much better solvent for a variety of solutes.

CO_2, aided by 'smart' molecules, such as surfactants, dendritic polymers and chelating agents, will affect a wide range of industries. It can be used to replace freons or

methylene chloride (or other chlorinated liquids) in cleaning operations. It can remove metals and other hydrophilic contaminants from waste water, soils and sludges. It can be used for emulsion polymerizations. It might be able to extract a pharmaceutical product from a fermentation broth, or provide a 'microreactor' with a controlled intramicellar environment for bioreactions. More importantly, all of these processes can be followed by a relatively easy separation step, which allows the reuse of an emerging environmentally friendly solvent. □

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1. Cooper, A. I. *et al. Nature* **389**, 368–371 (1997).
2. Roberts, C. B., Chateauneuf, J. E. & Brennecke, J. F. *Am. Inst. Chem Eng. J.* **41**, 1306–1318 (1995).
3. Morgenstern, D. A. *et al.* in *Supercritical Carbon Dioxide as a Substitute Solvent for Chemical Synthesis and Catalysis* (eds Anastas, P. T. & Williamson, T. C.) 132–151 (Am. Chem. Soc. Symp. Ser. 626, Washington DC, 1996).
4. Brennecke, J. F. *Chem. Ind.* No. 21, 831–834 (1996).
5. Yazdi, A. V. & Beckman, E. J. *Ind. Eng. Chem. Res.* **35**, 3644–3652 (1996).
6. Dillow, A. K. *et al. Ind. Eng. Chem. Res.* **35**, 1801–1806 (1996).
7. Johnston, K. P. *et al. Science* **271**, 624–626 (1996).
8. Clarke, M. J. *et al. J. Am. Chem. Soc.* **119**, 6399–6406 (1997).

Inhibitory synapses

Anaesthetics set their sites on ion channels

N. P. Franks and W. R. Lieb

The way in which volatile and gaseous general anaesthetics work has remained a puzzle ever since they were introduced into clinical practice during the 1840s. The prevailing view has been that anaesthetics (and, indeed, alcohol) do not have specific molecular targets in the conventional pharmacological sense, but that they nonspecifically disrupt nerve-membrane lipids[1,2]. Evidence in support of this includes the molecular simplicity of the agents, and the correlation of potency with fat solubility.

Although this idea is, in some ways, an attractive unifying concept, it has fallen out of favour: anaesthetic effects on lipid bilayers are very small, and the potencies[3] and stereo-selectivities[4] of general anaesthetics can be much more plausibly interpreted in terms of their binding directly to protein targets. Now, on page 385 of this issue, Mihic *et al.*[5] report another step towards identifying specific molecular sites on ion channels, which may be involved in the actions of general anaesthetics and ethanol.
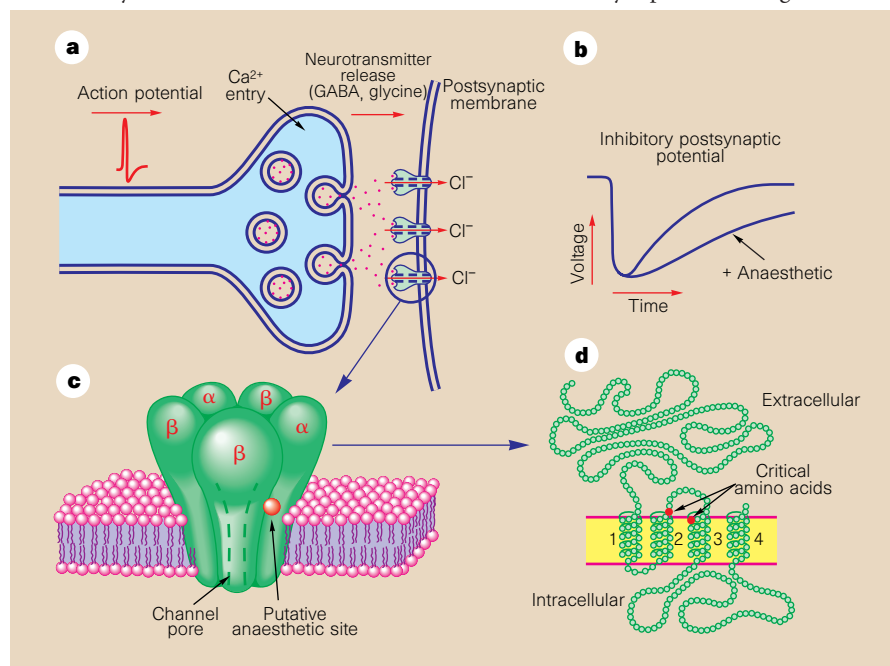
Chemical synapses are thought to be the

Figure 1 Mihic *et al.*[5] have found that single amino-acid substitutions at two positions remove the potentiating effects of volatile anaesthetics and ethanol on $GABA_A$ (γ-aminobutyric acid) and glycine receptors. a, $GABA_A$ and glycine receptors bind the neurotransmitters that are released at inhibitory chemical synapses, and open to allow chloride ions to diffuse across the postsynaptic membrane. b, The main effect of volatile anaesthetics is to prolong channel opening and, hence, to increase postsynaptic inhibition. c, The receptor channels consist of pentamers of closely related subunits, and the structure of a single subunit is shown in d. The authors suggest that the two critical amino acids may form a binding site for general anaesthetics and ethanol.