NATURE

100 YEARS AGO

We learn from the *Lancet* that the use of Röntgen rays as a means of certifying the existence of death was demonstrated at a recent meeting of the Biological Society of Paris. M. Bougarde showed three photographs of the thorax, two of them from living persons and the third from a corpse, all taken by the X-rays. In the two first the different thoracic organs and the walls of the thorax itself exhibited a hazy outline, so that their limits could not be exactly made out. This, of course, was owing to the natural movements of the parts, the pulsations of the heart and the great vessels, and the movements of the diaphragm. Even when the subjects held their breath so as to minimise movement as much as possible the outlines were still hazy. … In the radiograph of the corpse, however, the appearance was quite different, for all the organs had sharp and well-defined edges.

From *Nature* 19 May 1898.

50 YEARS AGO

Although lip-service is commonly paid to the value of research, it is seldom that its direct benefits are so attractively displayed to the general public as has been done in the "Darkness into Daylight" Exhibition at the Science Museum, London, S.W.7. … We are all of us aware of the progress and achievements made during the past century. But how many realize that since only 1921 the efficiency of the ordinary 60-watt electric lamp has increased by 55 per cent while the cost has decreased by 75 per cent. … We can see the dawn of electric lighting with Swan's invention of 1878, its temporary eclipse by the Welsbach incandescent gas mantle and then the final triumph of the electric filament lamp. … As is perhaps inevitable, the accent of the Exhibition is on fluorescent lighting, and as one passes through this section one is forced to wonder whether the life of the filament lamp is doomed and whether it will eventually be replaced, like the oil lamp and the gas lamp before, by the low-pressure fluorescent tubes now being so widely used. Hitherto, these fluorescent lamps have only been available in lengths of 4 and 5 ft., but the recent announcement that 2-ft. tubes of 20- and 40-watt ratings will soon be introduced suggests a much wider application for domestic purposes.

From *Nature* 22 May 1948.

Reverse pharmacology based on orphan GPCRs is a unique opportunity for drug discovery, especially given that most known therapeutic agents have GPCRs as their main target. The approach has proved itself on four occasions — for nociceptin[5] (orphanin FQ)[8], lymnokinin[9], the orexins[10] and now the prolactin-releasing peptide(s). Considering that over 100 orphan GPCR sequences have already been identified, and that when the Human Genome Project is completed, hundreds, if not thousands, more will probably have beeen found[4], no doubt this approach will soon provide many new leader compounds for the pharmaceutical industry to convert into clinically effective agents. □

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Thermodynamics

Size is everything

R. Stephen Berry

We are familiar with how bulk matter melts and freezes, and know that a pure substance has a sharp, well-defined melting temperature at a given pressure. But in clusters of tens, hundreds or thousands of atoms, very different properties appear. The report by Schmidt *et al.* on page 238 of this issue[1] is the first quantitative demonstration of how the melting temperature of clusters depends sensitively on their size. The temperature varies in what appears to be a highly irregular pattern, a pattern not yet interpreted, and the challenge is now to discover the physical basis for this variation.

The very concept of 'a' melting temperature disappears for such atomic clusters; instead, they have 'melting ranges' of temperature, in which solid and liquid coexist. An earlier publication by this group[2] showed how the fragmentation pattern of clusters could reveal the relation between their internal energy and their temperature, and hence their heat capacity. This in turn demonstrated experimentally the long-predicted finite range of temperatures within which solid and liquid clusters may coexist[3,4]. The authors identified the temperature of the maximum heat capacity as the melting point, because this is approximately the temperature at which an ensemble of the clusters is half solid, half liquid.

A size dependence of the melting of sodium clusters was suggested four years ago[5]. Schmidt *et al.* now show that changing the size of sodium clusters by just a few atoms can change their melting temperature by tens of per cent. Why?

The temperature range for coexistence of solid and liquid clusters depends on atomic binding energy — the ease with which atoms can be set free from their lattice sites, to move diffusively or to vibrate. And the binding energies of small and medium-sized clusters do not increase monotonically with cluster size, because they depend on two 'shell effects'. One is the effect of geometric shells: regular polyhedra, especially icosahedra and decahedra, are exceptionally stable. The other is the effect of electronic shells, in which the exceptionally stable structures correspond to complete electron shells analogous to those responsible for the stability and inertness of the rare gases. These effects compete to determine maxima and minima in the binding energy of clusters as functions of their size[6]. So could it be that shell effects are causing the observed melting-temperature variation? Schmidt *et al.* consider this possibility, but conclude that neither shell effect is strong enough to account for the variations they measured in melting temperature.

What of the entropy change that accompanies the change of phase? At the point of a phase change in bulk matter, the internal energy change from solid to liquid, ΔU, must exactly balance the contribution of entropy to the total energy change, $T\Delta S$ (where T is the temperature, S the entropy). Only at temperatures and pressures where these two are equal can solid and liquid coexist in equilibrium — this is the relation that yields the coexistence curve of the solid–liquid phase diagram. At any temperature and pressure off the coexistence curve, the equilibrium ratio of solid to liquid *bulk* samples in an ensemble is so overwhelmingly favourable to one phase or the other that, if a system is at equilibrium, the unfavoured phase isn't seen. Only by using a trick such as supercooling a liquid can we reveal the local stability of the unfavoured phase.

In clusters, the equality of ΔU and $T\Delta S$ ensures that the solid and liquid forms of the cluster are equally likely to be found. But the equilibrium ratio of liquid to solid clusters need not be unity for the two phase-like forms to coexist in observable quantities.

The changing slope of the internal energy U with temperature, over many tens of degrees Kelvin, displays this coexistence quantitatively for the first time in an experiment. The key to interpreting how these ranges, as well as the points of maximum slope of $U(T)$, vary with size, will come with understanding just what kinds of motion the atoms of liquid-like clusters can undergo.

Another challenge lies ahead. The theory of phase changes predicts that there are sharp limits to the band of coexistence, at any fixed pressure[3,4]. There should be a lower temperature limit, below which the liquid has not even local stability, and an upper limit, above which the solid has no local stability. Determining whether these sharp bounds exist will be difficult, requiring careful scrutiny of how the internal energy and heat capacity change as the conditions move into the coexistence region. It may well be that clusters of some sizes will show sharp thermodynamic changes and others will show more gradual changes. The clusters with the highest melting temperatures and highest coexistence temperatures will probably be those with the sharpest changes in heat capacity, because these will be the clusters for which the onset of melting is the most abrupt, in terms of the rate at which the increase in the entropic contribution makes the liquid become a locally stable form to compete with the lower-energy solid.

It is exciting to see experimental studies of the phase changes of clusters go beyond the demonstration that liquid and solid forms exist. Such investigations may do even more than reveal the fundamental character of phase changes. They open the possibility of exploring stable, phase-like forms of clusters — some like conventional solids, some floppy, some possibly unlike any normal forms of bulk solids — that cannot exist as equilibrium forms of bulk matter, and thence to the possibility of preparing and using nanoscale materials with structures unique to small systems, structures with properties that we select and design. □

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Behavioural ecology

Cuckoos beg the answer

Rory Howlett

Bawling babies are the bane of many long-suffering parents. But consider the lot of a pair of birds that spends weeks building a nest, and preparing to raise a brood of their own, only to be hoodwinked into caring instead for a gluttonous interloper. That is the fate of victims of the common cuckoo, *Cuculus canorus*. Cuckoos are brood parasites: rather than building nests of their own, they lay their eggs in the nests of other species, relying on the unwitting foster parents to incubate the egg and feed the hatchling until it is fully fledged. But why do the hosts put up with it? Therein lies a sinister and unlikely tale, as told by Nicholas Davies and colleagues in *Proceedings of the Royal Society*[1].

Davies *et al.* are interested in the battle of wits between the cuckoo and one of its host species, the reed warbler *Acrocephalus scirpaceus*. They studied a breeding population of about 300 reed warbler pairs in and around Wicken Fen near Cambridge in England. Reed warblers are vulnerable to cuckoos, and in some years at Wicken nearly a quarter of their nests are parasitized, although in other years only 1–2% of nests are affected. Female cuckoos surreptitiously lay a single egg in an unguarded nest. Adult reed warblers reject eggs that are unlike their own, and their powers of discrimination have been honed by natural selection. But in this coevolutionary arms race, the cuckoo has also been selected to lay eggs which beautifully mimic those of its hosts, and which are often accepted and incubated[2].

Paradoxically, cuckoo chicks are apparently not actively rejected, although they differ in appearance from the chicks of the host species. Not only does the impostor escape detection, it ejects the hosts' own eggs and hatchlings from the nest, with the foster parents often looking on helplessly. Why hosts tolerate these natural-born killers is perplexing, but theory has suggested that learning to recognize cuckoo chicks may be maladaptive for hosts[3]. Thus, if first-time breeders misimprint on a parasitic chick, thereby failing to recognize future offspring as their own, the costs of nestling recognition could outweigh the benefits in terms of lifetime reproductive success.

Whatever the case, cuckoo nestlings are more than tolerated. Although the foster parents are presented with just a single mouth gape rather than a nest full of gapes of their own young, they strive to provide the ravenous cuckoo chick with a copious supply of caterpillars and insects, leading to rapid growth. Grotesquely, the reed warbler ends up being dwarfed by the chick it is feeding (Fig. 1).

To find out how a cuckoo chick stimulates its foster parents to provide so much food, Davies *et al.* used some neat tricks. To test whether large size is sufficient to stimulate high provisioning rates, they temporarily replaced reed warbler broods with a single blackbird (*Turdus merula*) or song thrush (*T. philomelos*) chick. The surrogate chicks were accepted but were fed less food than cuckoo chicks of similar body mass. So size alone is not the key.

Perhaps cuckoo chicks are just expert beggars. The cuckoo chick has an unusual begging call, which Davies *et al.* describe as a

DAVID KJAER/BBC NATURAL HISTORY UNIT

Figure 1 **Fed up — cuckoo chick with a reed warbler surrogate parent.**