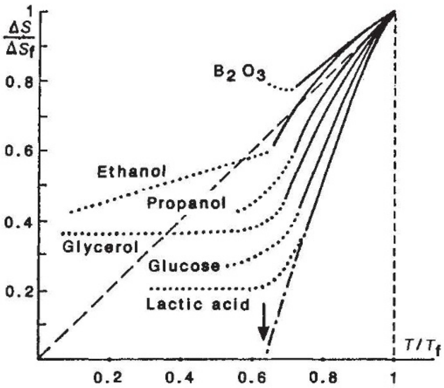
Kauzmann went on to advance reasons why, if a glass could maintain its configurational equilibrium down to the critical or 'Kauzmann' temperature at which its entropy equals that of the crystal, it would be forced to crystallize instantly. This is a paradox because at such low temperatures atomic diffusion is extremely sluggish so that crystallization should be impossible. Of course, as Kauzmann pointed out, the paradox is actually a metaphysical one, because it would be kinetically impossible for a glass to maintain configurational equilibrium down to such a low temperature. But the Kauzmann paradox continues to fascinate glass theorists and they continue to discuss its implications[3,4].

It has long been recognized that, whereas a liquid can be metastably super-



Variation of entropy (normalized with respect to the entropy of fusion) with temperature (normalized with respect to the freezing point). Solid curves, liquids in equilibrium; dotted curves, glassy state. Arrow, isentropic temperature for lactic acid. (Based on Kauzmann's data, from ref. 8.)

cooled, sometimes through hundreds of degrees, so long as heterogeneous nucleation can be discouraged (for example, by dividing up the melt into tiny discrete droplets), normally a crystal cannot be metastably superheated by more than a fraction of a degree. It can be superheated briefly, of course, while latent heat flows into the solid, but such a kinetic transient has nothing in common with metastable superheating. More recently, it has been recognized that melting, like freezing, is usually nucleated heterogeneously, at surfaces or interfaces (see my News and Views article[5]), and when special tricks are employed to prevent this then substantial superheating is feasible, for instance with noble-gas crystallites embedded epitactically in a metal crystal.

Fecht and Johnson discuss in this issue[1] whether there is an intrinsic limit to such superheating, just as the Kauzmann paradox sets an intrinsic — albeit metaphysical — limit to the supercooling of a glass. They follow Kauzmann in seeking to locate an isentropic temperature, T_i^s at which the entropies of the superheated crystal and the liquid phase are equal.

Fecht and Johnson calculate the entropy of superheated crystalline aluminium. It turns out that the role of lattice vacancies is crucial. Their concentration increases with rising temperature; if their contribution to entropy is neglected, then T_i^s coincides with the melting point, T_m, and superheating would be excluded. Taking the configurational entropy of vacancies into account yields an isentropic temperature (also the crystalline instability temperature) of 1,292 K = $1.38T_m$. (Fecht and Johnson's Fig. 1 on page 50 of this issue shows the result of the calculation; both upper and lower isentropic temperatures appear, the latter being the one associated with the Kauzmann paradox.)

If the vibrational entropy associated with vacancies is also allowed for, T_i^s comes out a little lower, at 1,234 K. An isenthalpic temperature (1,217 K) can also be calculated; above this temperature, melting is no longer heat-flow limited. Indeed, it is hard to see what can prevent a crystal from spontaneously melting in the narrow temperature range between the isenthalpic and the isentropic temperatures.

The vacancy concentration at the instability temperature is found to be as high as 6–7 per cent. This calls to mind earlier experimental and theoretical results (mostly due to Górecki; see my News and Views article[6]) suggesting that melting is correlated with the achievement of a critical vacancy concentration (taken to be less than 1 per cent by Górecki). But the effective vacancy (hole) concentration in an equilibrium melt at the melting point is estimated at around 10 per cent, and one way of regarding the isentropic catastrophe at $1.38T_m$ is that the solid becomes unstable against spontaneous collapse because of the high vacancy concentration. Fecht and Johnson express this by pointing out that at this temperature, the specific volumes of the liquid and of the superheated crystal become identical.

The authors conclude their stimulating *jeu d'esprit* by extending their instability concept from a pure metal to a solid solution, and present a hypothetical entropy diagram which shows T_i^s as a function of solute concentration.

The notion of what is in effect an upper absolute instability limit for the existence of a crystalline structure is a novel one: perhaps the closest parallel is the concept of an upper absolute instability limit for a first-order order–disorder transition[7]. □

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Daedalus

Tricks of the trade

Because the real world has few economically significant cyclic variations, business cycles must ultimately derive from human psychology. The big global cycles are probably too remote from individual business decisions to be easily explained; but Daedalus has hopes of understanding the small-scale fluctuations of small groups of businesses. DREADCO's economists are studying a specific case — a group of companies all competing to sell particular products in the same market: one of DREADCO's markets, in fact. The team is Fourier-transforming past records of sales, prices and so on, into their equivalent 'economic spectra'.

Each frequency peak in a firm's spectrum will correspond to some characteristic mechanism within it. Thus a two-year cycle may indicate how long a manager takes to disown his previous opinions; a one-year component may reveal the period over which a new technical advance comes to seem routine. Peaks shared by two companies show the influence of one firm on another: in fact the DREADCO team's final model of the system resembles a net of coupled oscillators.

The point of this laborious exercise is to initiate a new and subtle form of economic warfare. Somewhere in the spectrum of each of his rivals, says Daedalus, there should be a strong peak corresponding to some quite unstable attribute — some optimism or pessimism, some expansionist or defensive outlook poorly coupled to material reality, through which that rival is vulnerable. The economic model should soon reveal what behaviour on DREADCO's part (a periodic shift in pricing structure at the crucial frequency, maybe) will drive the rival concern into hopeless and uncontrollable resonant oscillation, until it goes bankrupt at one of the extremes of swing.

But what will happen when Daedalus's rivals realize the trick and try to play it on him? His defence is simple: bureaucracy. This damps and delays all organizational change. Too little, and wild instabilities are possible; too much, and the system cannot respond adequately to change. So Daedalus is sabotaging DREADCO's computer net, inserting formal paperwork and bumbling committees at strategic points, making the firm critically damped in all modes of oscillation. It will then have the minimum response-time consistent with stability.

Thus DREADCO's whizz-kid rivals will bite the dust, victims of their own heedless modernism: while DREADCO itself, like many other apparently old-fashioned organizations, will continue on its stately path into the future. David Jones