At MIT, Li et al.[2] have refined torque magnetometry — essentially a mechanical measurement of the force exerted on a magnet by an applied field — to a remarkable degree of sensitivity, and determined quantitatively the field and temperature dependence of the magnetization. They found a ferromagnetic state with magnetization values corresponding to the alignment of about two-thirds of the density of electrons expected from the polar catastrophe (values somewhat smaller than those found by Ariando et al.[12] in samples grown under similar conditions). Resistivity measurements show that the sample is also superconducting.

On the opposite coast, at Stanford, Bert et al.[3] used a scanning SQUID (superconducting quantum interference device) magnetometer to image the coexisting magnetic and superconducting states on the scale of a few micrometres. The superconductivity is inhomogeneous, with the superconducting regions occupying only a small fraction of the areas measured. The magnetic regions are similarly inhomogeneous, with patches of micrometre-scale ferromagnetic regions coexisting with a higher density of much smaller scale domains of fluctuating local magnetic moments. Remarkably, the total density of magnetic moments was found to be approximately equal to the density of electrons implied by the polar catastrophe. This is consistent with the finding of Sing et al.[11] that at the (001) $LaAlO_3/SrTiO_3$

interface most of the carriers needed to compensate for the polar discontinuity go into localized states, and strongly suggests that it is these states that give rise to the magnetization.

The results are all, broadly speaking, consistent, and it is worth pointing out that although in some of the studies[2,8,10,11] the materials used all came from the same source, others[3,12,13] are based on samples prepared in three different labs. A host of questions, however, remain to be answered. The relation between sample-preparation conditions and the occurrence of magnetism and superconductivity needs to be unravelled. Although the general picture of a polar-discontinuity-induced electron gas seems to be confirmed, the degree to which defects permit the existence of mobile electrons farther from the interface remains unknown. The cause — disorder or a many-body effect — of localization of the high density of carriers at the interface must be determined. The reliability of the calculations that indicated ferromagnetism requires investigation, and other mechanisms must be considered. And indeed, nagging quantitative discrepancies between the different experiments remain to be understood.

The simultaneous occurrence of ferromagnetism and superconductivity — two phases normally believed to be incompatible — will continue to attract attention, although the growing evidence for spatial inhomogeneity may indicate that the two phases simply live apart from each

other. Most importantly, the confirmation in different ways by Ariando et al.[12], Li et al.[2] and Bert et al.[3] of the ferromagnetism first hinted at by Brinkman et al.[9] marks the passing of a milestone. We now know that an oxide interface can exhibit an electronic phase (ferromagnetism) that has not been observed in either component material separately. This success should stimulate the search for other novel phases in other oxide-interface systems — and mark the beginning of a more intensive phase of research in the field of oxide interfaces. ❑

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GLASS PHYSICS

Prigogine and Defay say relax

For an important class of liquids, relaxation dynamics are constrained by a surprisingly simple scaling relationship between density and temperature. It seems that thermodynamics holds the key to pinning down the exponent.

C. Austen Angell and Iolanda Santana Klein

The behaviour of viscous liquids as they approach their glass-transition temperature, T_g, can be intriguing indeed. Simple Arrhenius plots of viscosity suggest that near T_g the energy cost of a molecule flowing past its immediate neighbours exceeds that of converting it to vapour — but the Arrhenius law proves to be invalid near T_g for such liquids. Minor increases in density can likewise effect spectacular changes in viscosity near T_g: whereas at a temperature of $3T_g$, large volume changes

have little effect on viscosity, a 1% change in density at $1.1\,T_g$ can cause the liquid to jam solid.

Fortunately, the past decade has seen an impressive advance in our understanding of viscous liquid dynamics. A number of studies[1,2] have demonstrated that, for many liquids, the effects of pressure (via density ρ) and temperature (T) on the relaxation time are constrained to vary according to a single scaling variable ρ^γ/T, where γ is the so-called density scaling exponent. Although surprising, this development

was a welcome simplification of the complex relaxation phenomenology. And now, in Nature Physics, Gundermann and colleagues report[3] that this density scaling exponent can be predicted from a combination of purely thermodynamic quantities. Even more astonishing is their revelation that the relevant thermodynamic quantity is a refined (linear) version of one of the oldest combinations of individually measureable thermodynamic response functions in the glass literature, the Prigogine–Defay (PD) ratio[4,5].

The classical PD ratio (Π), which is unity at an Ehrenfest second-order thermodynamic transition, is

$$\Pi = \Delta C_p \Delta \kappa_T / VT\Delta\alpha^2$$

where C_p, κ_T, and α are the heat capacity at constant pressure, isothermal compressibility and isobaric expansivity, respectively, and the Δ symbols denote the part of each response function in excess of the fixed structure (or glassy) value measured at T_g. Since the 1950s[4–7], the PD ratio has been seen as an indicator of complexity — a number suggesting the degree to which the thermodynamic state of the liquid fails to be described by a single order parameter ($\Pi = 1$). Gundermann et al.[3] reveal that the complexity implied by low PD ratios reflects the fact that the most widely studied liquids fail to meet the criteria for 'strongly correlated liquids' — that is, liquids in which pressure and temperature fluctuations occur in spatial and temporal unison[8,9]. Such liquids, they argue, should become the focus of the search for understanding of the glass problem at the deepest level[10]. Furthermore, a detailed review of all liquids examined thus far (in Fig. 3 of the paper[3]) reveals those best suited to the task. Aside from the tetramethyl-tetraphenyl-trisiloxane studied by Gundermann and colleagues, the only molecular liquid of this class that has been even approximately evaluated, is the model fragile liquid, orthoterphenyl (OTP).

It is ironic that this development coincides with a growing tendency in theoretical quarters to assign a trivial role to thermodynamics in relation to glass physics[11,12] and to concentrate on the mechanisms of particle motion, particularly facilitated dynamics, within the Kinetic Ising or East models. The present development would seem, then, to throw down the gauntlet on this issue.

Gundermann and colleagues[3] present a persuasive case; however, there are some outstanding issues. The PD ratio is usually obtained from the changes in the response function as the system 'breaks ergodicity' at the glass transition while cooling at some fixed rate (say 20 K min⁻¹) around temperatures for which the system relaxation time is about 100 s. The researchers, however, obtain the PD ratio by determining both real and imaginary parts of the three (frequency-dependent) response functions and then taking the slow component values used in this assessment at more or less
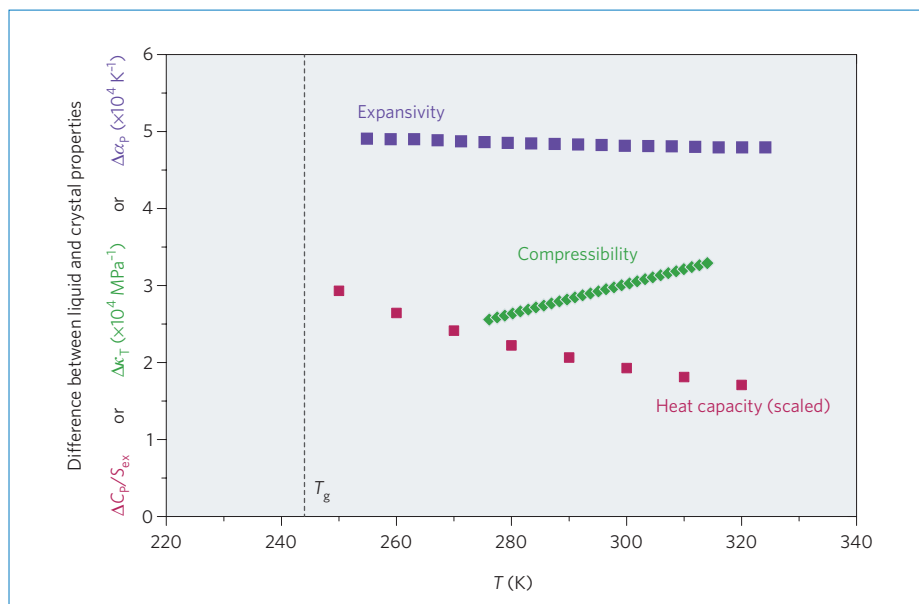

Figure 1 | Excess heat capacity (ΔC_p), expansivity ($\Delta\alpha_p$) and compressibility ($\Delta\kappa_T$) of liquid over crystal for OTP. As T_g is approached from above, $\Delta\kappa_T$ deceases to compensate increasing ΔC_p. Note that where κ_T and α are self-scaled by the volume ($\alpha = 1/V\,\partial V/\partial T$), the heat capacity is not, and acceptable methods of scaling are yet to find consensus. To avoid such ambiguity we scale by the excess entropy (liquid over crystal) to give a dimensionless variable, as in ref. 14.

the same frequency — corresponding to relaxation times of less than 1 s. This has the advantage that the system itself is in an ergodic state as the PD ratio is assessed (as is the case in a dielectric relaxation measurement, for instance). However, many independent studies have shown that these slow ('configurational' or better, 'excess') components of the response functions depend on temperature, particularly in the case of the excess heat capacity, which often increases sharply as T_g is approached from above. This quite naturally raises questions as to whether the PD ratio is single-valued, like the density scaling exponent. In fact, herein lies another welcome surprise.

Although thermodynamic data for glass formers, particularly compressibility data, are sparse, OTP is an exception, and the data for glass, crystal and liquid states[13] are sufficient to show that as the excess heat capacity increases, the excess compressibility compensates by decreasing, while the excess expansivity stays constant (Fig. 1). The PD ratio, like the density scaling exponent, is thus more or less independent of temperature in this case. Whether or not this is merely fortuitous in the case of OTP remains to be established by systematic studies, but a survey of the limited data available for van der Waals liquids reveals a temperature dependence of excess compressibility that

is rather generally opposite to that of the excess heat capacity. This observation further strengthens the findings of Gundermann et al., and hints at a correlation length for density fluctuations near T_g with temperature dependence opposite to that for the enthalpy fluctuations — promising fertile ground for future study. ❒

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