RESEARCH INTERESTS

Ian M Hodge

The areas of most interest to me are *The Glass Transition and Glassy State Relaxation*, and *Solid Electrolytes*.

The Glass Transition and Glassy State Relaxation

D. Weitz (Harvard): "There are more theories of the glass transition than there are theorists who propose them. It can get so controversial and [produce] so many loud arguments, and I don't want to get involved with that myself" [NY Times, July 29 2008].

S. Nagel (U Chicago): "Physics is really good at explaining problems that are linear, with clear borders, where all forces are local. But so much of everyday life is governed by systems that are not linear, not bordered, and not in equilibrium. Right beneath our nose there can be a deep physics problem" [Chicago Tribune, Jan 29 2008].

P. W. Anderson (Princeton), Nobel Laureate in condensed matter physics:

(a)"The deepest and most interesting unsolved problem in solid state physics is probably the theory of the nature of glass and the glass transition". [Science <u>267</u>, 1616 (1995)].

(b)"The spin glass ... requires a whole new version of statistical mechanics. Glass itself remains one of the deepest puzzles of physics" [Physics Today, p9 (July 1991)].

I am interested in the phenomenology of the kinetics of the glass transition, particularly those aspects that affect enthalpy relaxation and the associated kinetics of DSC scans ("structural relaxation"). My goal is to provide theorists with quantitative empirical information for them to explain. One of the most intriguing properties of the glass transition is the close relationship between its kinetic and thermodynamic aspects, but the thermodynamic aspects are controversial. It is my belief that a thermodynamic dimension cannot be denied – for example, homogeneous glasses that would be phase separated in the equilibrium super-cooled liquid state have constant kinetic T_g values over the composition range of phase separation. Also, there is often good agreement between the Ehrenfest relations for a thermodynamic second-order transition and experimentally observed relations for the thermal manifestations of the glass transition. The latter are disputed, but in my view largely because of inadequate consideration of uncertainties. The observed nonlinearity of {enthalpy, entropy, volume} relaxation implies that the relaxation times depend on {enthalpy, entropy, volume} (more on this below). My personal view is that if thermodynamics is dismissed as irrelevant then too large a body of agreement between thermodynamic and kinetic parameters must be dismissed as fortuitous.

Questions that require better answers include:

(1) What is the exact relationship between the kinetics of the glass transition and of glassy state relaxation? It is usually assumed, for very good reason but without precise quantitative justification, that these processes are the same. The difficulty is that the glass

transition is determined by longer time processes and glassy state relaxation by shorter time processes (thus the need to reduce temperature to make their time scale match that of the annealing time), and the issue of whether these are parts of the same distribution is not easily resolved. Stated otherwise, if the short time part of an assumed distribution were incorrect for the glass transition the description of the glass transition would not be compromised, but the description of annealing would be. There is good evidence that the short time components of the distribution governing the glass transition indeed determine the annealing distribution, because sub-T_g endotherms in annealed glasses with broad distributions for the glass transition are well accounted for. However, Johari-Goldstein processes have no heat capacity signatures and are almost unaffected by annealing, so if they are an integral part of the glass transition and annealing phenomena (still debated) then enthalpy relaxation does not reflect all the dynamic processes that contribute to the glass transition, as is often assumed.

(2) What is the fundamental theoretical basis of the nonlinear Adam-Gibbs ("Scherer-Hodge") phenomenology? Although imperfect it is probably the best extant account.

(3) How can enthalpy relaxation parameters be determined more accurately? Heat transfer effects in DSC scans need to be better incorporated into least squares fitting algorithms.

The glass transition has three canonical features ("the three nons"):

(1) <u>Non-Arrhenius Thermal Activation</u>: In the supercooled liquid state above the glass transition temperature range, a generally good description for the temperature dependence of the average structural relaxation time is given by the empirical Fulcher equation $\langle \tau \rangle = A \cdot \exp\left[B / \left(T - T_0 \right) \right]$, where A, B and T_o are empirical constants that yield an "effective activation energy" $E_{effective} / R = B / \left(1 - T_0 / T \right)^2$. This activation energy is termed "effective" because it often exceeds chemical bond strengths. The accepted interpretation of this fact is that many moieties must cooperatively rearrange for relaxation to occur and that this cooperativity produces non-Arrhenius behavior.

(2) <u>Nonexponentiality</u>: Usually well described by the "stretched exponential", "Kohlrausch-Williams-Watts" (KWW), or "Williams-Watt" (WW) function $\phi\left(t \right) = \exp\left[- \left(t / \tau \right)^{\beta} \right]$. I prefer the moniker WW. Nonexponentiality is expected for a cooperative relaxation process but the details are obscure. Nonexponentiality produces the memory effect (the dependence of relaxation not only on the initial state but also on how that state was reached). One result of the memory effect is that relaxation away from the equilibrium state can occur within some time intervals.

(3) <u>Nonlinearity</u>: This is observed when the system falls out of equilibrium. It is indicated experimentally by the finding that the relaxation/retardation time τ for any relaxing property $P(t)$ depends on the value of P - thus τ can also be expressed as a function of time as P relaxes. This is handled phenomenologically using the "reduced time" function

$\xi\ t\ \equiv \int_0^t dt'/\tau\ t'$ (where zero time is defined by the first departure from equilibrium),

and the nonlinear KWW function is used in the form $\phi\ t\ = \exp\ -\left[\xi\ t\ \right]^\beta$.

Nonlinearity is the focus of my interest. The best extant accounts of nonlinearity are provided by the "Tool-Narayanaswamy-Moynihan" (TNM) equation

$$\tau_0\ t\ = A_{TNM}\cdot \exp\left[\frac{x\cdot h}{R\cdot T\ t}+\frac{1-x\ \cdot h}{R\cdot T_f\ t}\right],$$ and the "Scherer-Hodge" (SH) relation

$$\tau_0\ t\ = A_{SH}\cdot \exp\left\{\frac{B}{T\ t\ \cdot\left[1-T_2/T_f\ t\ \right]}\right\}.$$ In these equations the fictive temperature, T_f,

is defined as the temperature at which the non-equilibrium value of property P would be the equilibrium value (its specific value of T_f depends in general on the property). Thus equilibrium is characterized by $T_f\ t\ =T\ t$, in which case the SH expression simplifies to the Fulcher relation with $T_2 = T_0$. The empirical quantity x in the TNM equation is unity for a completely linear process and zero for a totally nonlinear process. I have shown that the parameters in these quite different formalisms are related by $B \approx x^2h/R$ and $T_2 \approx T_g\ 1-x$, and these approximate relations have proven to be robust. The SH kinetic parameter T_2 (and corresponding Fulcher parameter T_0) is often about the same as the thermodynamic (Kauzmann) temperature T_K, at which the configurational entropy extrapolates to zero (within experimental uncertainties that can be large and are far too often not estimated). This provides a possible link between nonlinearity and thermodynamics, as mentioned above – thus one of the most fundamental kinetic aspects of the problem, nonlinearity, can plausibly be related to one of the most controversial issues of glass transition science – its thermodynamic aspects.

The two expressions for $T_f\ t$, as a function of thermal history $T\ t$ starting at an initial temperature T_i at which equilibrium prevails, are

$$T_f\ t\ =T_i+\int_{T_i}^{T}\left(1-\exp\left\{-\left[\int_0^t \frac{dt'}{A_{TNM}\cdot \exp\left[\frac{x\cdot h}{R\cdot T'\ t'}+\frac{1-x\ \cdot h}{R\cdot T_f\ t'}\right]}\right]\right\}\right)dT',$$

(TOOL-NARAYANASWAMY-MOYNIHAN (TNM))

and

$$T_f(t) = T_i + \int\limits_{T_i}^{T} \left(1 - \exp\left\{ -\left[\int\limits_{0}^{t} \frac{dt'}{A_{SH} \cdot \exp\left\{ \dfrac{B}{T'(t') \cdot \left[1 - T_2 / T_f(t') \right]} \right\}} \right] \right\} \right) dT'.$$

(SCHERER-HODGE (SH))

The nonlinearity of these expressions arises from $T_f(t)$ occurring in the innermost integrand, as indicated in red.

Solid Electrolytes

      I am a proponent of the complex electric modulus function M^*, defined as the reciprocal of the complex relative permittivity ε^*. The average relaxation time τ_D for M^* defines the time scale for relaxation of the electric field E at constant displacement D, which differs from the average retardation time τ_E that defines the time scale for relaxation of the displacement D at constant electric field E. When combined with the complex resistivity ρ^* the electric modulus can be used, inter alia, to obtain detailed information on intergranular impedances that is obscured by traditional complex permittivity and complex conductivity analyses. The complex electric modulus also has the useful property of suppressing high capacitance phenomena, such as electrode polarization and impedances associated with thin layers and electrochemical reactions (for which M^* is therefore unsuitable). Thus M^* is particularly suited for the analysis of electrical properties of heterogeneous materials, and for interfacial phenomena such as the Maxwell-Wagner-Sillers effect. The electric modulus M^* is controversial and I have co-authored a paper defending it and correcting misleading and incorrect statements in the literature. Essentially, it is impossible to physically distinguish between the electric current and the displacement current for ionic conductivity. They are easily separated experimentally (quadrature components of the complex conductivity or complex permittivity, see below), but their physical distinction is the issue that is debated. The following is distilled from a spirited email debate I have had about the validity of M^* (11/20/08):

    "The displacement current arises from localized ion hopping between adjacent sites - as is well known this gives rise to a Debye dielectric loss. The electric current arises from long range migration of ions, *but this migration must occur by a sequence of the same*

individual hops that produce the displacement current. The electric and displacement currents can easily be measured separately from the quadrature components of the complex resistivity $\rho*$ or complex permittivity $\varepsilon*$, but because of the conundrum just described their physical distinction is not obvious. My position, and that of Moynihan, Ngai, Angell, Williams, and many others, is that there is <u>no</u> physical distinction − they both arise from ion hopping between sites. This indistinguishability has experimental support, namely that the frequency at which $\varepsilon''_{residual} \equiv \varepsilon'' - \sigma_0 / e_0 \cdot \omega$ is a maximum tracks exactly with the inverse conductivity relaxation time defined by the limiting low frequency conductivity σ_0 - they both have identical activation energies for example. The *M** formalism is based on the idea that the electric and displacement currents arise from the same process of ionic hopping, and that their indistinguishability cannot be avoided. There is nothing wrong with this position - for example, the Maxwell equation for curl *H* does not distinguish between the electric and displacement currents. The occurrence of the limiting high frequency relative permittivity for the conductivity relaxation, ε_∞, in the relation between σ_0 and the conductivity relaxation time, is not problematic - polarizability has an obvious influence on ionic mobility."

Consider the atomic level limit of the Maxwell relaxation time $\tau = RC = e_0 \varepsilon_\infty / \sigma_0$. If this is equated to a vibrational lifetime (about 10^{-13} s) and $\varepsilon_\infty = 5$ (a typical value for ionic conductors), then $\sigma_{0,\max} \approx 9 \times 10^{-12} \quad 5 \,/ 10^{-13} = 450 \text{ S/m}$, which is close to the maximum observed ionic conductivity (single crystal beta alumina averaged over temperature) of about 500 S/m.

The equivalence of $\varepsilon*$ and $\sigma*$ is easily demonstrated using the Maxwell equation $\nabla \times H = J + \partial D / \partial t = \sigma E + e_0 \varepsilon \ \partial E / \partial t$. For an excitation $E = E_0 \exp \ -i\omega t$ this becomes

$$\nabla \times H = \sigma E_0 \cdot \exp \ -i\omega t \ -ie_0 \omega \varepsilon \cdot E_0 \cdot \exp \ -i\omega t$$
$$= E_0 \exp \ -i\omega t \ \left[\sigma - ie_0 \omega \varepsilon \right]$$
$$= E \left[\sigma - ie_0 \omega \varepsilon \right],$$

corresponding to a complex conductivity $\sigma* \ i\omega \ = \sigma' - i\sigma'' = \sigma' - ie_0 \omega \varepsilon'$. Equivalently,

$$\nabla \times H = e_0 \left(\frac{\partial E}{\partial t} \right) \left[\varepsilon + \frac{\sigma E}{e_0 \ \partial E / \partial t} \right]$$
$$= e_0 \left(\frac{\partial E}{\partial t} \right) \left[\varepsilon - \frac{\sigma}{ie_0 \omega} \right] \qquad ,$$
$$= e_0 \left(\frac{\partial E}{\partial t} \right) \left[\varepsilon + i\sigma \,/\ e_0 \omega \ \right]$$

corresponding to a complex relative permittivity $\varepsilon^* = \varepsilon' + i\varepsilon'' = \varepsilon' + i\sigma'/\ e_0\omega$. The complex resistivity ρ^* is defined by $\rho^* = 1/\sigma^* = 1/\ ie_0\omega\varepsilon^* \ = M^*/\ ie_0\omega$. The reciprocal relation between σ^* and ρ^* does not trouble anybody, so why then is the same reciprocal relation between ε^* and M^* anathema to some scientists?