<div align="center">**RESEARCH INTERESTS**
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The areas of most interest to me are:
(1) *The Glass Transition and Glassy State Relaxation*
(2) *Solid Electrolytes*.

(1) *The Glass Transition and Glassy State Relaxation*
P W Anderson (Princeton), Nobel Laureate in solid state physics:
(i) "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].
(ii) "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)].
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]
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]

I am interested in the phenomenology of the kinetics of the glass transition and glassy state relaxation (physical aging), particularly those aspects that affect enthalpy relaxation and the associated kinetics of DSC scans. One of the most intriguing properties of the glass transition is the close relationship between its kinetic and thermodynamic aspects. The thermodynamic aspects of the glass transition are controversial because they are mainly based on extrapolation. My personal view is that if thermodynamics is dismissed as irrelevant, then too large a body of agreement between thermodynamic and kinetic properties 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 often assumed, for good reason but without 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. There is solid evidence that the short time components of the distribution governing the glass transition do indeed determine aging, because sub-T_g endotherms in annealed glasses with broad distributions for the glass transition are well accounted for [see papers (18) and (20) in my publications list]. Also, 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 aging phenomena then enthalpy relaxation does not reflect all the dynamic processes that contribute to the glass transition.
(2) What is the theoretical basis of the phenomenology? The Non Linear Adam-Gibbs (NLAG) or Scherer-Hodge (SH) phenomenology is the best extant account, but it is imperfect.

(3) How can enthalpy relaxation parameters be determined more accurately? This has happily and significantly improved in recent yuears

The glass transition has three canonical features:
(1) Non-Arrhenius Thermal Activation;
(2) Non-exponentialily;
(3) Non-linearity.

(1) Non-Arrhenius Thermal Activation
 This gives rise to very large effective activation energies for the average retardation time in the supercooled liquid state immediately above the glass transition temperature range, A generally good description of the temperature dependence of the average relaxation time is given by the empirical Fulcher equation:

$$\langle \tau \rangle = A_F \exp\left[B / (T - T_0) \right],$$ (1)

for which the effective activation energy is

$$E_{effective} / R \approx B / (1 - T_0 / T)^2 .$$ (2)

The 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.

(2) Non-exponentiality
 This is usually well described by the "stretched exponential" or "Williams-Watts" (WW) function

$$\phi(t) = \exp\left[-(t/\tau)^\beta \right].$$ (3)

Non-exponentiality is expected for cooperative relaxation processes but the details are obscure.

(3) Non-linearity
 Within the glass transition temperature range, the Fulcher equation must be generalized to account for non-linearity when the system falls out of equilibrium. Nonlinearity is indicated by the experimental finding that the retardation time τ for any relaxing property $P(t)$ depends in part on the value of P - thus τ can also be expressed as a function of time as P relaxes. Nonlinearity is the focus of my interest. The best extant accounts of nonlinearity are the Tool-Narayanaswamy-Moynihan (TNM) and Scherer-Hodge (SH) expressions for the average retardation time for the fictive temperature T_f. The TNM expression is

$$\tau_0(t) = A_{TNM} \exp\left[\frac{xh}{RT(t)} + \frac{(1-x)h}{RT_f(t)} \right],$$ (4)

and the SH relation is

$$\tau_0(t) = A_{SH} \exp\left\{ \frac{B}{T(t)\left[1 - T_2 / T_f(t)\right]} \right\},$$ (5)

where T_f is the fictive temperature defined as the temperature at which the nonequilibrium value of some property P would be the equilibrium value - thus equilibrium is characterized by $T_f(t) = T(t)$. The quantity x ("nonlinearity parameter") is unity for a linear process. I have shown that the parameters in these apparently quite different formalisms are simply related:

$$B \approx x^2 h / R \tag{6}$$

and

$$T_2 \approx T_g(1-x). \tag{7}$$

According to the Adam-Gibbs model the kinetic parameter T_2 can be identified with the thermodynamic (Kauzmann) temperature T_K at which the configurational entropy extrapolates to zero. Thus one of the most problematic aspects of the glass transition kinetics, nonlinearity, can plausibly be related to one of the more controversial issues of glass transition science - its thermodynamic aspects.

Nonlinearity can be eliminated by the reduced time

$$\xi(t) \equiv \int_0^t \frac{dt'}{\tau(t')}, \tag{8}$$

where the lower limit of zero is determined by the time at which equilibrium is first lost. The reduced time linearizes the kinetics and allows the mathematical machinery of linear response theory to be used - in particular Boltzmann superposition can be applied. For example, the enthalpic fictive temperature for DSC scans for the TNM and SH expressions are

$$T_f(t) = T_i + \int_{T_i}^{T} \left(1 - \exp\left\{-\left[\int_0^t \frac{dt'}{A_{TNM} \exp\left[\frac{xh}{RT'(t')} + \frac{(1-x)h}{RT_f(t')}\right]}\right]\right\}\right) dT', \tag{9}$$

$$T_f(t) = T_i + \int_{T_i}^{T} \left(1 - \exp\left\{-\left[\int_0^t \frac{dt'}{A_{SH} \exp\left[\frac{B}{T'(t')\left[1 - T_2/T_f(t')\right]}\right]}\right]\right\}\right) dT'. \tag{10}$$

Nonlinearity in both equations is reflected by the occurrences of $T_f(t)$ in the innermost integrals.

(2) Solid Electrolytes.

I am a proponent of the complex electric modulus function $M*$, defined as the reciprocal of the complex relative permittivity $\varepsilon*$. The average relaxation time for $M*$ defines the time scale for relaxation of the electric field E at constant displacement D, that differs from the average

retardation time that defines the time scale for relaxation of the displacement D at constant electric field E. When combined with the complex resistivity, 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. Thus M^* is particularly suited for the analysis of electrical properties of heterogeneous materials. However, M^* is controversial and I have co-authored a paper [publication 38] defending it and correcting misleading and incorrect statements in the literature. Essentially, it is difficult to physically distinguish between the electric current and the displacement current for ionic conductivity. They can very easily be experimentally separated (quadrature components of the complex conductivity or complex permittivity), but their physical distinction is the central issue.

The following is distilled from an email debate I have had about the validity of M^*: "The displacement current arise from localized ion hopping between adjacent sites - as is well known this gives 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 conductivity or complex permittivity, but because of the conundrum just described their physical distinction is not obvious - the position of myself Moynihan, Ngai, Angell and many others is that there is NO physical distinction - they both arise from ion hopping between sites. This indistinguishability has experimental support, namely that the frequency at which $\varepsilon''_{residual} \equiv \varepsilon'' - \sigma_0 / e_0 \omega$ is a maximum tracks exactly with 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 they are indistinguishable. For example, the Maxwell equation $\nabla \times H = J + (\partial D / \partial t)$ does not distinguish between the electric and displacement currents. Consider the microscopic version of the Maxwell relaxation time $\tau = RC = e_0 \varepsilon_\infty / \sigma_0$. If τ is equated to a vibrational lifetime (10^{-13}) s and $\varepsilon_\infty = 5$ (a typical value for ionic conductors), then $\sigma_0^{max} \approx (10^{-11})(5) / 10^{-13} \approx 500\ \mathrm{Sm^{-1}}$, close to the maximum observed ionic conductivities (e.g. beta alumina) of about 300 $\mathrm{Sm^{-1}}$"

The equivalence of ε^* and σ^* is easily demonstrated using one of the Maxwell equations:
$\nabla \times H = J + (\partial D / \partial t) = \sigma E + e_0 \varepsilon (\partial E / \partial t)$. For an excitation $E = E_0 \exp(-i\omega t)$ this becomes
$$\nabla \times H = \sigma E_0 \exp(-i\omega t) - ie_0 \omega \varepsilon E_0 \exp(-i\omega t)$$
$$= E_0 \exp(-i\omega t)[\sigma - ie_0 \omega \varepsilon]$$
corresponding to a complex conductivity $\sigma^*(i\omega) = \sigma' - i\sigma'' = \sigma' - ie_0 \omega \varepsilon'$. Equivalently,

$$\nabla \times H = e_0 \left(\frac{\partial E}{\partial t} \right) \left[\varepsilon + \frac{\sigma E}{e_0 \left(\partial E / \partial t \right)} \right]$$

$$= e_0 \left(\frac{\partial E}{\partial t} \right) \left[\varepsilon - \sigma / i e_0 \omega \right] \tag{11}$$

$$= e_0 \left(\frac{\partial E}{\partial t} \right) \left[\varepsilon + i \sigma / e_0 \omega \right]$$

corresponding to a complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon' - i\sigma'/ e_0 \omega$. Thus $\sigma^* = i e_0 \omega \varepsilon^*$.