

RESEARCH INTERESTS

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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, Nobel Laureate in solid state physics (italics added):

(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 267 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 or interpret. One of the most intriguing properties of the glass transition is the apparent close relationship between its kinetic and thermodynamic aspects, but the thermodynamic aspects of the glass transition are controversial because they are almost all 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 parameters must be dismissed as fortuitous.

Questions that require better answers include:

(a) 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 strong 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 [papers (18) and (20) in list of publications]. 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. There may also be other short time processes that contribute to the kinetics of the glass transition or annealing but are not included in the current phenomenologies.

- (b) What is the theoretical basis of the phenomenology? The nonlinear Adam-Gibbs (“Scherer-Hodge”) phenomenology is the best extant account, but it is imperfect.
- (c) How can enthalpy relaxation parameters be determined more accurately?

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

Non-Arrhenius Thermal Activation

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 $\langle \tau \rangle = A \cdot \exp\left[B / (T - T_0)\right]$, where A , B and T_0 are empirical constants, which yields an "effective activation energy" given by $E_{eff} / R = B \cdot T^2 / (T - T_0)^2 = B / (1 - T_0 / T)^2$. 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.

Nonexponentiality

Usually well described by the "stretched exponential" or "Williams-Watts" (WW) function $\phi(t) = \exp\left[-(t/\tau)^\beta\right]$ ($1 \geq \beta > 0$). Nonexponentiality is expected for a cooperative relaxation process, but the details are obscure. The n^{th} moment of the average relaxation time for this function is $\langle \tau^n \rangle = \left\{ \tau_0^n / [\beta \cdot \Gamma(n)] \right\} \Gamma(n / \beta) = \left[\tau_0 / \Gamma(1+n) \right] \cdot \Gamma[1+n / \beta]$.

Nonlinearity

This is observed when the system falls out of equilibrium. It is indicated experimentally by the finding that the relaxation/retardation time 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. Nonlinearity is the focus of my interest. The best extant accounts of nonlinearity are provided by the "Tool-Narayanaswamy-Moynihan" (TNM) equation

$$\tau_0 = A \cdot \exp\left[\frac{x \cdot h}{R \cdot T} + \frac{(1-x) \cdot h}{R \cdot T_f}\right],$$

and the "Scherer-Hodge" (SH) relation

$$\tau_0 = A \cdot \exp\left[\frac{B}{T \cdot (1 - T_2 / T_f)}\right].$$

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 - thus equilibrium is characterized by $T_f(t) = T(t)$, in which case the SH expression simplifies to the Fulcher relation with $T_2 = T_K$. The quantity x in the TNM equation (nonlinearity parameter) is unity

for a completely linear process and zero for a totally nonlinear process. I have shown that the parameters in these apparently quite different formalisms are related by $B \approx x^2 \cdot h$ and $T_2 \approx T_g \cdot (1-x)$. These approximate relations have proven to be quite accurate. The SH kinetic parameter T_2 (and corresponding Fulcher parameter T_0) can also be identified with the thermodynamic (Kauzmann) temperature T_K at which the configurational entropy extrapolates to zero. Thus one of the most difficult kinetic aspects of the problem to handle, nonlinearity, can plausibly be related to one of the more 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 a temperature T_0 at which equilibrium prevails, are

$$T_f(t) = T_0 + \int_{T_0}^T \left\{ 1 - \exp \left[- \int_0^{t'} \frac{dt''}{A \cdot \exp \left[\frac{x \cdot h}{R \cdot T(t'')} + \frac{(1-x) \cdot h}{R \cdot T_f(t'')} \right]} \right] \right\}$$

TOOL-NARAYANASWAMY-MOYNIHAN (TNM)

and

$$T_f(t) = T_0 + \int_{T_0}^T \left\{ 1 - \exp \left[- \int_0^{t'} \frac{dt''}{A \cdot \exp \left\{ \frac{B}{T(t'') \cdot [1 - T_2 / T_f(t'')] \right\}} \right] \right\}$$

"SCHERER-HODGE"(SH)

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

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 for M defines the time scale for relaxation of the electric field E at constant displacement D , which differs from the average retardation time that defines the time scale for relaxation of the displacement D at constant electric field E (analogous to the relation Lyndon-Sachs-Teller between the frequencies of longitudinal and transverse optical phonons). 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. 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 (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), 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 ρ^* or complex permittivity ϵ^* , but because of the conundrum just described their physical distinction is not obvious. The position of myself, Moynihan, Ngai, Angell, Williams and many others is that there is NO physical distinction — they both arise from ion hopping between sites. This indistinguishability has direct experimental support, namely that the frequency at which $\epsilon''_{residual}$ 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 is inevitable. There is nothing fundamentally 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 at all problematic — polarizability has an obvious influence on ionic mobility. Consider the atomic level version of the Maxwell relaxation time $\tau = R \cdot C = e_0 \cdot \epsilon_\infty / \sigma_0$. If τ is equated to a vibrational lifetime (10^{-13} s) and $\epsilon_\infty = 5$ (a typical value for ionic conductors), then $\sigma_{0,max} \approx (9 \times 10^{-12})(5) / 10^{-13} \approx 450$ S/m, which is close to the maximum observed ionic conductivities (beta alumina) of about 300 S/m."

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

$$\begin{aligned}
\nabla \times H &= \sigma \cdot E_0 \cdot \exp(-i \cdot \omega \cdot t) - i \cdot e_0 \cdot \omega \cdot \varepsilon \cdot E_0 \cdot \exp(-i \cdot \omega \cdot t) \\
&= E_0 \cdot \exp(-i \cdot \omega \cdot t) \cdot [\sigma - i \cdot e_0 \cdot \omega \cdot \varepsilon] \\
&= [\sigma - i \cdot e_0 \cdot \omega \cdot \varepsilon] \cdot E
\end{aligned}$$

corresponding to a complex conductivity $\sigma^* = \sigma' - i \cdot \sigma'' = \sigma' - i \cdot e_0 \cdot \omega \cdot \varepsilon'$. Equivalently,
 $\nabla \times H = -i \cdot e_0 \cdot \omega \cdot \varepsilon \cdot E_0 \cdot \exp(-i \cdot \omega \cdot t) \cdot [\varepsilon' - \sigma' / i \cdot e_0 \cdot \omega] = [\varepsilon' - \sigma' / i \cdot e_0 \cdot \omega] \cdot \partial D / \partial t$,
corresponding to a complex relative permittivity $\varepsilon^* = \varepsilon' + i \cdot \varepsilon'' = \varepsilon' - \sigma' / i \cdot e_0 \cdot \omega$. Thus
 $\sigma^* = i \cdot e_0 \cdot \omega \cdot \varepsilon^*$. The complex resistivity ρ^* is defined by
 $\rho^* = 1 / \sigma^* = 1 / (i \cdot e_0 \cdot \omega \cdot \varepsilon^*) = M^* / (i \cdot e_0 \cdot \omega)$. The reciprocal relation between σ^* and ρ^*
does not trouble anybody. Why then is the same reciprocal relation between ε^* and M^* so
problematic for so many scientists?