CHAPTER FOUR (11)
STRUCTURAL RELAXATION
[NO FIGURE DRAFT]

Table of Contents

4.1 Introduction

Structural relaxation refers to changes in the kinetic and thermodynamic properties of nonequilibrium amorphous materials as they approach the amorphous equilibrium state (i.e. not a crystal) and is intimately related to the glass transition phenomenon and glassy state relaxation. A large portion of this chapter is accordingly devoted to thermodynamics and to the glass transition phenomenon. The principle difference between the kinetics of structural relaxation and the other relaxations considered in earlier chapters is that the underlying phenomena are less well characterized and are often based on extrapolations. They are not understood at anywhere near the level of electrical and visco-elastic relaxations - there are no Maxwell equations nor Newton's laws for succor for example. This issue essentially arises from the central role played by temperature because "everything changes with temperature". Structural relaxation is strongly nonlinear because the average structural relaxation time depends on the thermodynamic state as well as on temperature – thus the isothermal relaxation time changes as relaxation towards thermodynamic equilibrium proceeds. Mathematically this is handled by making the average relaxation time a function of time and replacing the elapsed time with the reduced time defined below.

Structural relaxation is most significant within and near the glass transition temperature range that is often but misleadingly referred to as the "glass transition temperature" T_g. Typically T_g is defined as lying within the glass transition temperature range (often but not always midway) and this tradition is followed here until definitions of the glass transition temperature are discussed in 4.8.3.1. Essentially "T_g" will be used as an abbreviation for "glass transition temperature range".

4.1.1 Nomenclature

The SI unit for temperature (Kelvin, symbol K) is just as fundamental as those for mass, length and time so that, for example, 1000K = 1kK. Constant pressure processes are referred to as isobaric, those at constant volume as isochoric, and those at constant temperature as isothermal as is usual). The convention that intensive properties such as pressure and temperature are written in lower case and extensive properties such as volume, enthalpy, entropy, heat capacity etc., are written in upper case is *not* followed here as is often done in textbooks. The principle reasons for this are that an exception must always be made for temperature T to avoid confusion with the time t and that units indicate the distinction anyway (per kg or per mole for extensive quantities for example). Boltzmann's constant is written as k_B and the ideal gas constant is written as R as is customary. The symbol τ is used for a relaxation time considered as a variable and τ_0 refers to any characteristic relaxation time as a parameter in expressions such as the nonexponential WW decay function.

4.2 Elementary Thermodynamics

Thermodynamics is fraught with subtleties that require extensive study to master so the present exposition is necessarily simplified and abbreviated. Recommended books on the subject include Fermi [1] (terse), Lewis and Randall [2] (aimed at physical chemists) and Landau & Lifshitz [3] (aimed at physicists). Be aware that [3] dispenses with Boltzmann's constant (for good reason) so that T in many of its formulae should be replaced with k_BT to make contact with common usage – this conversion has been made for the formulae from [3] cited below.

4.2.1 Temperature Scales

Four scales are extant: Fahrenheit (^{o}F), Celsius or Centigrade (^{o}C), Rankine (^{o}R), and Absolute or Kelvin (K). Only the Kelvin scale is used in thermodynamics (and in most of science for that matter) but ^{o}C is occasionally used, especially in the chemical and material science literatures. Only in the US is the Fahrenheit scale used in everyday use.

The Celsius and Fahrenheit scales are defined by the melting (T_m) and boiling (T_b) temperatures of water at atmospheric pressure. For the Fahrenheit scale T_m is 32^{o}F and T_b is 212^{o}F the values of which have historical empirical roots: 0^{o}F was originally defined to be the lowest temperature at which water could be frozen when a salt was added (thus in the US the sodium chloride most often used for ice/snow melting is only effective down to single digit Fahrenheit temperatures), and 100^{o}F was defined to be the average temperature of human blood. These values have since been modified to simplify the conversion between the Fahrenheit and more objective Celsius scales. For the Celsius scale T_m is defined to be 0^{o}C and T_b is 100^{o}C. Thus the difference (T_b - T_m) is 100^{o}C and 180^{o}F, and after accounting for the 32^{o} difference at T_m the equations for conversion between the Fahrenheit (F) and Celsius (C) scales are

$$\begin{aligned} C &= \left(F-32\right)/1.80, \\ F &= 1.80C+32. \end{aligned} \tag{4.1}$$

The temperature at which the two scales are numerically equal is therefore -40^{o}.

The R and K scales are based on the lowest possible temperature being zero (for the justification of such an absolute zero see any introductory physics or physical chemistry text as well as [1] - [3]). The absolute Kelvin scale is based on the experimental result that such an absolute zero occurs at -273.15^{o}C and the Rankine scale is based on an absolute zero that occurs at about -460^{o}F.

4.2.2 Quantity or Amount of Material

The most common metric is the mole whose unit is the *mol* and equals Avogadro's number $N_A = 6.02\times10^{23}$. Even although the mole is a pure number it is useful to keep track of it as if it had the unit mol because it is clearly and importantly different from just the number of particles being considered. It is important to be extra careful when using the mol because the question "mol of what" needs to be addressed. For example the gaseous phase of the element sulfur consists of molecules such as S_2, S_4, S_6 and S_8 so that per mol of sulfur is ambiguous.

4.2.3 Gas Laws and the Zeroth Law of Thermodynamics

The ideal gas equation is

$$PV = nRT = Nk_BT \tag{4.2}$$

where P is pressure, V is volume, T is temperature, N is the number of entities, and n is the number of moles. Equation (4.2) can be derived from what is probably the most basic application of statistical mechanics to a collection of perfectly elastic spherical particles of insignificant volume (see any introductory physics or physical chemistry text). A noteworthy result of this statistical mechanical analysis is

$$\overline{KE} = \frac{3}{2}nRT \tag{4.3}$$

where $\overline{KE}$ is the average kinetic energy per mole of particles. Equation (4.3) provides a fundamental interpretation of temperature – it is a measure of the average energy of all N molecules (for an ideal gas the kinetic energy is entirely translational but in general includes vibrational and rotational degrees of freedom). This equivalence is discussed in [3] and is the reason that k_B is omitted from its equations. A definition of temperature was recognized to be logically necessary well after the 1st and 2nd Laws had been established and the adopted definition is therefore referred to as the zeroth law of thermodynamics: "If C is initially in thermal equilibrium with both A and B, then A and B are also in thermal equilibrium with each other. Two systems are in thermal equilibrium if and only if they have the same temperature".

Van der Waals improved the ideal gas equation by introducing two corrections: (i) The finite volume of the particles is subtracted from the volume of the system – thus V in the ideal gas equation is replaced by $(V - nb)$ where b is an empirical constant reflecting the nonzero particle volume. (ii) Attractive (van der Waals) forces between the particles reduce the gas pressure because of two factors: (a) The average momentum per particle is reduced in proportion to (n/V), thus reducing the impulsive force per particle arising from each reflection from the walls of the container; (b) the reduction in total momenta is proportional to the product of the reduction per particle and the number density (n/V) of particles. Thus the pressure is reduced in proportion to (n^2/V^2) and the Van der Waals equation becomes

$$\left(P - an^2/V^2\right)(V - nb) = RT, \tag{4.4}$$

where a is another empirical constant. The latter depends in part on the polarizability α of the particles because of the theoretical van der Waals interaction (London) potential L between identical particles separated by a distance r

$$L = -\left(\frac{3}{4}\right)\frac{hv\alpha^2}{(4\pi e_0)^2 r^6}, \tag{4.5}$$

where h is Planck's constant, v is the Bohr ground state orbiting frequency and hv is the energy of the Bohr ground state. An excellent heuristic derivation of the London potential has been given by Israelachvili [4] using the (polarizable) Bohr atom (this derivation is acknowledged to be based on an account by Tabor that is unfortunately not referenced). The Israelachvili/Tabor result differs from eq. (4.5) only by the constant (1.00 rather than 0.75).

Equation (4.4) is a cubic equation in *V* that can rationalize the first order transition from gas to liquid (using the Maxwell construction) when gas particles have an attractive force between them (see any introductory physics and physical chemistry textbook).

4.2.4 Heat, Work and the First Law of Thermodynamics

As noted above the temperature of an ideal gas is proportional to the average kinetic energy per ideal gas particle [eq. (4.3)] ("thermal energy"). Heat (*Q*) is thermal energy in transit that spontaneously flows from a system of higher thermal energy (higher *T*) to that of lower thermal energy (lower *T*). The reverse process requires an input of energy (work *W*) defined by

$$W = \int_{V_1}^{V_2} P(V)\,dV \,. \tag{4.6}$$

The temperature of any material is a measure of its internal energy *U* [a generalization of eq. (4.3)] and the balance of heat transfer *Q*, *U* and work *W* is given by the *First Law of Thermodynamics*:

$$U = Q + W \tag{4.7}$$

that is valid for all systems and not just for ideal gases. Equation (4.7) is beholden to yet another sign convention because as written it requires that *W* be defined as positive for work done *on* the system. Another convention regards *W* as positive for work done *by* the system and the sum on the right hand side of eq. (4.7) then becomes a difference. There is also more to eq. (4.7) than its algebra because although both *Q* and *W* depend on the path taken from one state to the other their sum *U* is independent of the path. Path invariant functions such as *U* are often called *state functions*.

4.2.5 Entropy and the Second Law of Thermodynamics

The path dependence of $Q = \int_A^B \delta Q$ is eliminated by dividing all heat transfers δQ by the temperature *T* at which each transfer occurs. The quantity $\delta Q/T$ is the change in entropy *dS* and the state function entropy *S* is given by

$$S = \int_A^B \frac{\delta Q}{T} = \int_A^B dS \,. \tag{4.8}$$

Entropy is not generally conserved (except for adiabatic processes for which $\delta Q = 0$ and for idealized equilibrium processes) and actually increases for irreversible processes. It is therefore a unique scientific function because not only is it not generally conserved but it increases for spontaneous processes when it is not. Consider for example the spontaneous transfer of a quantity of heat *Q* from a body *A* at temperature T_A to another body *B* at a lower temperature T_B. The entropy of the two bodies together increases because the entropy Q/T_A lost by *A* is smaller than the entropy Q/T_B gained by *B*. This analysis depends of course on neither heat nor matter (with its internal energy *U*) entering or leaving the system consisting of $A+B$, and on no work being done on or by the system - the system $A+B$ is then said to be closed or isolated. The *Second Law of Thermodynamics* states that for all processes taking place in a closed system the total change in entropy ΔS is greater than or equal to zero:

$$\Delta S \geq 0 \tag{4.9}$$

where the equality obtains only for adiabatic and idealized equilibrium processes.

The statistical mechanics of Boltzmann yields a simple relation between the entropy *S* of a system and the number Ω of possible configurations available to the system:

$$S = k_B \ln \Omega \tag{4.10}$$

where k_B is Boltzmann's constant = R/N_A (although it was Planck who introduced it, not Boltzmann [5]). Thus more probable states have higher entropies so that eq. (4.10) provides an interpretation of the Second Law – systems naturally migrate to states with more configurations that have a greater probability. The kinetics of such migrations is a major theme of this chapter. The largest practical problem with applying eq. (4.10) is obtaining an expression for Ω - most often this cannot be done even for idealized model systems. None other than Einstein gave a lot of thought to eq. (4.10) as well as several other statistical mechanical matters such as fluctuations. Einstein's contributions to and analyses of statistical physics and thermodynamics are discussed in Chapter 4 (entitled "Entropy and Probability") of what this author regards as the definitive biography of Einstein [5].

4.2.6 Heat Capacity

The increase in a body's temperature *dT* for any given heat input δQ is determined by the body's isobaric and isochoric heat capacities C_p and C_v

$$\begin{gathered} C_p = \left(\frac{\partial Q}{\partial T}\right)\Bigg|_P \text{ and} \\ C_v = \left(\frac{\partial Q}{\partial T}\right)\Bigg|_V, \end{gathered} \tag{4.11}$$

where lower case is used for all subscripts and δQ has been replaced by dQ to indicate that the heat transfer is direct and not dependent on path. Heat capacities per unit mass are too often referred to as "specific heats" that is confusing and misleading (what prevents the use of "specific heat capacities"?). Heat capacities have the same units as entropy but the two are physically very different: entropy is a process-dependent quantity related to heat transfer at a particular temperature or a material-dependent quantity related to the randomness of the material, whereas heat capacity is a material property that refers to the change in temperature for a given heat input that is independent of the randomness of the material and does not depend on how heat is input to the material.

The isobaric and isochoric heat capacities differ because at constant pressure some of the heat input produces an increase in volume that does work on the environment [eq. (4.6)] and therefore reduces any increase in the internal energy *U* and temperature *T* so that $C_p \geq C_v$, specifically [2]

$$C_P - C_V = \frac{\alpha^2 TV}{\kappa_T} \geq 0 \tag{4.12}$$

where

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P \tag{4.13}$$

is the isobaric expansivity and

$$\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{4.14}$$

is the isothermal compressibility. Mechanical stability demands that $\kappa_T > 0$ so that eq. (4.12) ensures $C_p \geq C_v$ because *V* and *T* are positive definite and α^2 is necessarily positive even when α is negative (supercooled water for example). It can be shown [6] that α for solids arises from odd number vibrational harmonics (even numbered harmonics do not). The isobaric heat capacity C_P is almost always considered in this chapter, an exception being the theoretical Einstein and Debye heat capacities discussed next.

4.2.7 Debye Heat Capacity and the Third Law of Thermodynamics

Quantum phenomena affect $C_p(T)$ and $C_v(T)$ at low temperatures. Einstein (Chapter 20 of [5] entitled "Einstein and Specific Heats") was the first to apply quantum considerations to the heat capacity and consequently was the first to deduce that $\lim_{T\to 0} C_v(T) = 0$ although his result that $\lim_{T\to 0} C_v(T) \propto T$ is quantitatively incorrect. Debye extended Einstein's result by introducing a distribution of phonon (collective vibrational quanta) energies rather than Einstein's heuristic assumption of a single energy. The Debye result for *N* "atoms" (no internal degrees of freedom) is [6]

$$C_V\left(T\right) = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} \left\{\frac{x^4 \exp(x)}{\left[\exp\left(x\right)-1\right]^2}\right\} dx \quad \left(x_D = \theta_D / T\right) \tag{4.15}$$

where Θ_D is the Debye temperature corresponding to a maximum cutoff energy for the distribution of phonon energies. For $T \rightarrow 0$ the parameter $x_D \rightarrow \infty$ and the integral in eq. (4.15) is a calculable constant so that $\lim_{T\to 0} C_v(T) \propto T^3$. The T^3 behavior is observed for crystalline materials but not for glasses for which $\lim_{T\to 0} C_V(T) \propto T$. The latter has been rationalized in terms of two state models [6] but is not understood at a fundamental level because the two states are unknown. In both cases however it remains true that $\lim_{T\to 0} C_v(T) = 0$ so that the entropy

$\lim_{T\to 0} S = \lim_{\delta T\to 0} S\int_0^{0+\delta T} C_v d\ln T$ is also zero and eq. (4.10) then implies that $\Omega = 1$ and there is only one possible state at 0 K. This is the basis of the *Third Law of Thermodynamics* (originally called the Nernst Theorem), one the best expressions of which is probably that by Fermi [1]:

> "…to the thermodynamical [sic] state of a system at absolute zero there corresponds only one dynamical state of lowest energy compatible with the given crystalline structure, or state, or state of aggregation of the system".

Immediately after that definition Fermi adds an important comment:

> "The only circumstance under which Nernst's theorem might be in error are those for which there exist many dynamical states of lowest energy [i.e. degeneracy]. But even in this case the number of states must be enormously large (of the order of $\exp(N)\ldots$) if the deviations from the theorem are to be appreciable. Although it is not theoretically impossible to conceive of such systems, it seems extremely unlikely that such systems actually exist in nature".

Some sort of "ideal glass" with an energy degenerate number of configurations much fewer than $\exp(N)$ at 0 K is perhaps a candidate for a "not theoretically impossible" state. Perhaps even "sufficiently small" deviations from an ideal mathematically degeneracy (energy levels with "sufficiently small" differences) could qualify for such a state.

4.3 Thermodynamic Functions

4.3.1 Entropy S

$$dS = \frac{\delta Q}{T}. \tag{4.16}$$

As with eq. (4.7) for the First Law there is more to equation (4.16) than just the algebra. The use of δQ rather than dQ indicates that as noted above in §4.2.2.4 the total heat $\int_A^B \delta Q$ transferred to or from the system from state A to state B is path dependent but the total entropy change $\Delta S = \int_A^B dS$ is not.

4.3.2 Internal Energy U

This is defined by eq. (4.7). In terms of the other thermodynamic functions defined here:

$$dU = TdS - PdV. \tag{4.17}$$

4.3.3 Enthalpy H

Defined as

$$\begin{aligned} H &= U + PV; \\ dH &= \left(TdS - PdV\right) + \left(VdP + PdV\right) \\ &= TdS + VdP. \end{aligned} \tag{4.18}$$

Enthalpy relaxation is discussed in detail later in this chapter.

4.3.4 Free Energies *A* and *G*

Free energies are thermodynamic potentials (defined as such in [3]) because systems are driven to decrease their free energies. The Helmholtz free energy A and Gibbs free energy G correspond to isochoric and isobaric conditions respectively:

$$\begin{aligned} &A = U - TS, \\ &dA = -PdV - SdT, \end{aligned} \tag{4.19}$$

$$\begin{aligned} &G = H - TS = U + PV - S \\ &dG = VdP - SdT. \end{aligned} \tag{4.20}$$

The negative sign of the TS term in eqs. (4.19) and (4.20) signifies that systems are in part driven to equilibrium by increasing their entropy. The other term signifies that systems are also driven to decrease their energy U or H. It is the balance of these potentially conflicting drives that defines the eventual direction of a process or reaction, as illustrated by the thermodynamics of DNA helix formation: it is energetically heavily favored by hydrogen bonding between base pairs but entropically expensive because it is more ordered compared with the disorder of separated strands and more disordered ambient water molecules. Reproduction of life therefore depends on the small difference between a large enthalpy factor and entropy factors that are readily modified near room temperature by molecular environment.

4.3.5 Chemical Potential μ

For a species i this quantity is denoted by μ_i and is needed when the number of different entities in a system is not constant. Let this variable number be n_i for species i. Then [3]

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V} = \left(\frac{\partial W}{\partial n_i}\right)_{S,P}. \tag{4.21}$$

Which derivative is chosen simply changes the variables in which μ_i is expressed – for example if G is chosen the variables are $\{P, T\}$ and if A is chosen the variables are $\{V, T\}$. The entities can be atoms, molecules, ions, even electrons. For charged entities the electrostatic potential $z_i e\varphi$ must be added to μ_i to give the electrochemical potential μ_i^E

$$\mu_i^E = \mu_i + z_i e\varphi \tag{4.22}$$

(z_i is the charge on the entity i in electron charges, e is the (positive) electron charge, and φ is the electrostatic potential). In solid state physics μ_i^E is the Fermi energy ϵ_F of electrons.

For a system of just one species the chemical potential is simply a thermodynamic potential (A, G) per entity [3]. For example when the G derivative in eq. (4.21) is chosen then

$$d\mu = -sdT + vdP \tag{4.23}$$

where s and v are the entropy and volume per entity (cf. eq. (4.20)). It is important to note that eq. (4.23) does not apply to an individual entity – it simply expresses the macroscopic quantities in eq. (4.20) in different units (per particle rather than per mole of particles). Thermodynamics cannot be applied to single entities because its functions are averages and standard deviations (fluctuations) for macroscopic numbers of entities (in statistical mechanics the limit of an infinite number of entities is referred to as the "thermodynamic limit").

4.3.6 Internal Pressure

Defined as $T\left(\partial S/\partial V\right)_T$ and motivated by

$$dU = -PdV + TdS, \tag{4.24}$$

$$\Rightarrow \left.\frac{\partial U}{\partial V}\right|_T = -P + T\left(\frac{\partial S}{\partial V}\right)_T . \tag{4.25}$$

4.3.7 Derivative Properties

Properties that are defined in terms of the first or second derivatives of free energy with respect to temperature, pressure or volume are often referred to as first or second order functions. For example

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T , \tag{4.26}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T , \tag{4.27}$$

and

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P \tag{4.28}$$

are first order functions and C_p eq. (4.11), C_v eq. (4.11), α eq. (4.13), and κ_T eq. (4.14) are second order functions. In addition to eq. (4.12) the difference between C_p and C_V is also given by

$$C_P - C_V = \left.\left(\frac{\partial H}{\partial T}\right)\right|_P - C_V = \left.\left(\frac{\partial U}{\partial T}\right)\right|_P + \left.\left(\frac{\partial\left(PV\right)}{\partial T}\right)\right|_P - C_V . \tag{4.29}$$

4.4 Maxwell Relations

The Maxwell relations relate the derivatives of various thermodynamic functions. For example

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V , \tag{4.30}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \Leftrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V , \tag{4.31}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P . \tag{4.32}$$

Other relations can be obtained from other applications of differential forms. For example

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right) \tag{4.33}$$

obtained from

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_T \Rightarrow \left(\frac{\partial C_p}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial P \partial T}\right) \tag{4.34}$$

so that

$$\left(\frac{\partial S}{\partial P}\right)\Big|_T = -\left(\frac{\partial V}{\partial T}\right)\Big|_P \Rightarrow \left(\frac{\partial^2 S}{\partial P \partial T}\right) = -\left(\frac{\partial^2 V}{\partial T^2}\right)\Big|_P . \tag{4.35}$$

Another example is [2]

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P . \tag{4.36}$$

Many other relations can be derived from the Jacobeans (§1.6) arising from changes in thermodynamic variables. A summary of these formulae is given in [2].

4.5 Fluctuations

Thermodynamic functions F are defined by averages $\langle F \rangle$ over large numbers of entities (e.g. eq. (4.3)). These averages have corresponding variances $\langle F^2 \rangle$ and standard deviations $\langle F^2 \rangle^{1/2}$ that are referred to as "fluctuations". These fluctuations have thermodynamic significance because many of them are related to thermodynamic functions. For example [3]

$$k_B C_p = \langle \Delta S^2 \rangle \tag{4.37}$$

and

$$k_B T V \kappa = \langle \Delta V^2 \rangle . \tag{4.38}$$

Fluctuations have kinetic implications because quantities fluctuate in time and the fluctuations at time t and a later time $t + T$ can be correlated [3]. Thus fluctuations are of obvious relevance to relaxation phenomena in general and structural relaxation in particular. The correlation for a quantity x is defined by

$$\phi(T) = \overline{x(t)x(t+T)} \tag{4.39}$$

where the average is over a distribution of probabilities. As T increases to infinity any "memory" of the state at time t will decay to zero so that $\lim_{T\to\infty} \phi(T) = 0$.

4.6 Egodicity

This is a statement of the equivalence of probabilities in terms of time averages and various ensemble averages in statistical mechanics. The differences between the various ensembles are beyond the scope of this elementary introduction apart from stating their variables: canonical (n, V, T), micro-canonical (n, V, U), and grand canonical (μ, V, T). The essence of ergodicity is illustrated by a simplified traffic analogy. For the analogy to be good it is required to assume that all drivers on the road behave the same (much less likely than assuming all molecules act alike). Consider the probability of a driver doing something such as turning with no turn signal to indicate intent ("event" hereafter). There are two ways to evaluate the probability that such an event will occur:

(i) Observe traffic behavior in a restricted area (a county say) for a "very long time" and find the probability that the event occurs (say 10%). A "very long time" is loosely defined as the minimum observation time for which longer observation times would not change the probability.

(ii) Observe all traffic patterns over the country for an "instant" and average them to obtain the probability of no turn signals.

The ergodic hypothesis asserts that these two probabilities are the same (10%). However if the time of observation in (i) is too short to include all possibilities then ergodicity is said to be broken and the time average will be less than 10%. This occurs in the glassy state where relaxation times of years or even millennia are confidently estimated and longer observation times are impractical. The glass transition phenomenon is correctly said to be "ergodicity breaking" but it is incorrect to assert that ergodicity breaking is equivalent to a glass transition (see discussion of the Deborah Number below and the article by Angell [7]). Such assertions ignore the details and subtleties of the glass transition phenomenon. A more rigorous discussion of ergodicity is given in [5] (Chapter Four "Entropy and Probability") from which the following is taken. Two definitions by Boltzmann are given. The first, dating from 1868, considers the evolution in time of a closed system of N particles in orbit on a surface of constant energy in $6N$-dimensional space. A particular state S_i then corresponds to a point i on the orbit. Now observe the system for a long time T and determine the time T_i for which it is in the state S_i. Then $\lim_{T\to\infty}\left(T_i/T\right)$ is the probability that the system is in state S_i. Einstein independently re-introduced this definition in 1903 and was his favored definition. Boltzmann's second definition was to calculate the number of ways w of partitioning n_i particles each with energy $\in_i$ under the constraints that the total energy $E=\sum n_i \in_i$ and $N=\sum n_i$ are fixed and (crucially) that the particles are in practice distinguishable (not so quantum mechanically). Boltzmann then proposed that w was proportional to the probability of any distribution of $\{n_i\}$ values. The first definition is in principle observable but the second is, in Pais's words, "more like a declaration". Ergodicity asserts that Boltzmann's two definitions are equivalent and again as Pais [5] stated "This [equivalence] is the profound and not yet fully solved problem of ergodic theory".

The Deborah number DN [8] is defined as the ratio of the characteristic timescale of the observed system (typically a relaxation time) and of the measurement timescale. For an applied sinusoidal perturbation the timescale of observation corresponds to the period of oscillation. The glass transition occurs when the DN passes through unity with changing temperature – for example during rate cooling through the glass transition temperature range (abbreviated by "T_g" as noted in §4.1). Above T_g relaxation times are less than 100 s or so and longer observation times are easily achieved. As noted above relaxation times of years or even millennia are confidently estimated below T_g and observation times are necessarily much smaller. The DN is also usefully defined as [8]

$$DN \equiv \frac{d\tau}{dt} = \left(\frac{d\tau}{dT}\right)\left(\frac{dT}{dt}\right) = \left(\frac{d\tau}{dT}\right)Q_c = 1 \tag{4.40}$$

where Q_c is the cooling rate (the heating rate is not recommended because for DSC scans the kinetics of recovery are partly determined by the previous thermal history -- see [8] for details.

4.7 Phase Transitions

These are transitions between different states (phases) of a material. A useful classification scheme for them was introduced by Ehrenfest who proposed that discontinuous changes in a property defined by the n^{th} derivative of a thermodynamic potential (free energy A or G) be termed an n^{th} order transition. Thus melting and boiling for which first order properties such as V, H and S are discontinuous are 1st order transitions. Transitions for which second order properties such as the heat capacity C_p or C_v, expansivity α or compressibility κ are discontinuous are 2nd order transitions, and so on. The Ehrenfest classification is imperfect – for example λ transitions in metal alloys are referred to as second order transitions but do not fall into Ehrenfest's classification. Nonetheless it is useful to discuss the glass transition phenomenon in terms of an Ehrenfest 2nd order "transition".

First some nomenclature. Thermodynamic relations are applied below and above the transition temperature and the difference between thermodynamic functions is denoted by Δ. Thus for an Ehrenfest 2nd order transition $\Delta V = \Delta H = \Delta S = 0$ because the transition is not first order. The various first derivatives of ΔV, ΔH and ΔS are not zero however because by definition an Ehrenfest 2nd order transition exhibits discontinuities in these derivatives. The pressure dependencies of an Ehrenfest second order transition temperature T_2 for different thermodynamic functions are readily derived using elementary calculus. For volume

$$d\Delta V = 0 = \left(\frac{\partial \Delta V}{\partial T}\right)_P dT + \left(\frac{\partial \Delta V}{\partial P}\right)_T dP = V\left(\Delta\alpha dT - \Delta\kappa_T dP\right) \tag{4.41}$$

from which

$$\left(\frac{\partial T_2}{\partial P}\right)_V = \frac{\Delta\kappa_T}{\Delta\alpha} \tag{4.42}$$

where eqs. (4.13) and (4.14) for $\Delta\alpha$ and $\Delta\kappa_T$ have been used. Deviations from eq. (4.42) have often been reported but O'Reilly [9] has pointed out that $\Delta\kappa_T$ is strongly pressure dependent and that reasonable values can be found for it that agree with eq. (4.42).

For enthalpy

$$d\Delta H = \left(\frac{\partial \Delta H}{\partial T}\right)_P dT + \left(\frac{\partial \Delta H}{\partial P}\right)_T dP = \Delta C_p dT + \left[\Delta V - T\left(\frac{\partial \Delta V}{\partial T}\right)_P\right] dP = 0 \tag{4.43}$$

but since $\Delta V = 0$ then

$$\left(\frac{\partial T_2}{\partial P}\right)_H = VT\frac{\Delta\alpha}{\Delta C_p}. \tag{4.44}$$

For entropy

$$\begin{aligned} d\left(\Delta S\right) = 0 = \left(\frac{\partial \Delta S}{\partial T}\right)_P dT + \left(\frac{\partial \Delta S}{\partial P}\right)_T dP = \left(\frac{\partial \Delta S}{\partial T}\right)_P dT - \left(\frac{\partial \Delta V}{\partial T}\right)_T dP \\ = T^{-1}\Delta C_p dT - V\Delta\alpha dP \end{aligned} \tag{4.45}$$

so that

$$\left(\frac{\partial T}{\partial P}\right)_{\Delta S} = VT\frac{\Delta\alpha}{\Delta C_p}. \tag{4.46}$$

Note that eqs. (4.44) and (4.46) are the same.

In anticipation of the nonlinear Adam-Gibbs model for structural relaxation an expression for $\partial T / \partial P$ based on TS_c being constant is desirable. The condition that TS_c be constant implies $d\left(TS_c\right) = TdS_c + S_c dT = 0 = \Delta C_p dT - TV\Delta\alpha dP + S_c dT = \left(\Delta C_p + S_c\right)dT - TV\Delta\alpha dP$ so that

$$\left(\frac{\partial T_2}{\partial P}\right)_{TS_c} = VT\frac{\Delta\alpha}{\Delta C_p + S_c}. \tag{4.47}$$

The Prigogine-Defay ratio Π is defined by

$$\Pi \equiv \frac{\left(\partial T / \partial P\right)\big|_{\Delta V}}{\left(\partial T / \partial P\right)\big|_{\Delta S}} = \frac{\Delta C_p \Delta\kappa_T}{TV\left(\Delta\alpha\right)^2}. \tag{4.48}$$

It has been shown by Davies and Jones [10] that if $\Pi > 1$ then more than one thermodynamic variable must determine the transition. Values of $\Pi > 1$ have often been reported but McKenna [11] has suggested that the usually quoted values of $\Delta\alpha$, $\Delta\kappa_T$ and ΔC_p are not obtained under the proper conditions and that if they were then Π could be unity within uncertainties. If one variable is chosen for convenience to determine relaxation behavior then entropy is evidently better than volume because entropy and enthalpy can accommodate things that volume cannot such as bond angle constraints and stresses that are known to affect glassy state relaxation rates and are presumably factors in liquid relaxation as well.

4.8 Structural Relaxation

An excellent account of this topic is given by C. A. Angell et al. [12] that lists questions that need answering and the then current best answers (essentially unchanged to this day). It also considers other topics such as ionic conductivity in glasses that are discussed in Chapter Two of this book. The following section is divided into three sections arranged according to three temperature ranges relative to T_g: (1) $T > T_g$ (supercooled liquids); (2) $T < T_g$ (glasses); (3) $T \approx T_g$ (glass transition).

4.8.1 Supercooled Liquids and Fragility

Supercooled liquids are precursors to glasses formed by cooling through the glass transition temperature range and their properties are therefore relevant to structural relaxation. Relaxation times in supercooled liquids (and many liquids above the melting temperature) rarely adhere to the Arrhenius temperature dependence

$$\tau_0(T) = A_A \exp\left(\frac{E_a}{RT}\right) \tag{4.49}$$

where E_a is the Arrhenius activation energy and A_A is a constant. Instead they (including water) generally adhere to relations that are often well approximated by the Fulcher equation (see [13] for an excellent discussion of its history and [14] for a reprint of the original paper):

$$\tau_0(T) = A_F \exp\left(\frac{B_F}{T - T_0}\right), \tag{4.50}$$

where A_F, B_F and T_0 are positive constants independent of temperature but material dependent. The effective Arrhenius activation energy E_{eff} for the Fulcher relation is

$$\left(\frac{E_{eff}}{R}\right) = \left[\frac{d\ln\tau_0}{d(1/T)}\right] = \left[\frac{B_F}{(1 - T_0/T)^2}\right]. \tag{4.51}$$

Other expressions for $\tau_0(T)$ are discussed in [12] but we select one here for further discussion because it is frequently used in the polymer community – the WLF equation:

$$\log_{10} a_T \equiv \log_{10}\left[\frac{\tau(T)}{\tau(T^*)}\right] = \frac{C_1(T - T^*)}{\left[T - (T^* - C_2)\right]} \tag{4.52}$$

where T^* is a reference temperature that is usually equated to the glass transition temperature T_g and C_1 and C_2 are constants that depend on T^* however. The WLF parameters C_1 and C_2 are related to the Fulcher parameters B_F and T_0 by

$$T_0 = T^* - C_2 \tag{4.53}$$

and

$$B_F = 2.303 C_1 C_2 \tag{4.54}$$

where the factor 2.303 arises from the irritating use of $\log_{10}$ rather the natural ln. Equations (4.53) and (4.54) indicate why C_1 and C_2 are T^* dependent because T_0 is an objective measure of departure from Arrhenius behavior [eq. (4.51)]. The value of C_1 for $T^* = T_g$ is "universally" about 17 for polymers but C_2 is material dependent. The relation between the Fulcher and WLF parameters and Angell's fragility scheme [CAAP] is discussed immediately below.

A fruitful characterization of supercooled liquids is the classification scheme of fragility introduced by Angell. This scheme has been developed over many publications and is not amenable to a definitive citation (although [15,16] are useful and [17] includes a list of references). Reference [17] criticizes some mathematical issues related to fragility but these criticisms do not detract from the immense overall value of the concept. A probable correlation between fragility and the canonical nonlinearity of structural relaxation is discussed below.

There are two complementary definitions of fragility, thermodynamic and kinetic, that intimate the intricate but debated relation between the thermodynamic and kinetic aspects of the glass transition. This relation is the basis of the Adam-Gibbs model [18] discussed below. The thermodynamic definition is the origin of the term fragility and defines it in terms of the isobaric heat capacity change $\Delta C_p\left(T_g\right)$ over the glass transition temperature range: large values of $\Delta C_p\left(T_g\right)$ imply large increases in the configurational entropy with increasing temperature above T_g that in turn imply a large decrease in structural order and therefore a more fragile structure. The kinetic definition of fragility is essentially a quantitative statement of the generally observed positive correlation between $\Delta C_p\left(T_g\right)$ and the departure from Arrhenius behavior of $\tau_0\left(T\right)$ that as noted above is generally well described by the Fulcher equation. Its definition was originally expressed in terms of the Fulcher equation but it has since been more usefully and generally defined in terms of a fragility parameter m that is essentially a T_g-scaled effective Arrhenius activation energy at T_g that is independent of the form of $\tau_0\left(T\right)$:

$$m \equiv \left.\frac{d\log_{10}\left(\tau_0\right)}{d\left(T_g/T\right)}\right|_{T=T_g} = \frac{E_{eff}}{RT_g}. \tag{4.55}$$

This corresponds to the slope at $T = T_g$ of the "Angell plot" $\log_{10}\left(\tau_0\right)$ versus T_g/T. The limiting values of τ_0 are determined by the plausible boundary conditions $\tau_0 = 10^2$ s at $T \approx T_g \Rightarrow T_g/T \approx 1$ and $\tau_0 = 10^{-14}$ s (vibrational lifetime) as $T \to \infty \Rightarrow T_g/T \to 0$.

The minimum value $m_{\min}$ of the fragility index is the minimum slope of the Angell plot obtained by connecting the two extrema of τ_0 with a straight (Arrhenius) line. For the boundary conditions given above

$$m_{\min} = \log_{10}\left[\frac{\tau_0\left(T_g\right)}{A_A}\right] = 2-\left(-14\right) = 16. \tag{4.56}$$

The quantity A_A in eq. (4.56) refers specifically to the Arrhenius equation (4.49) and not to any other equation for $\tau_0\left(T\right)$ that has a pre-exponential factor that is generically and confusingly often just termed A in the literature. To ensure that the argument of the logarithm function is explicitly dimensionless the following modified form is useful:

$$m' \equiv \left.\frac{d\log_{10}\left(\tau_0/A_A\right)}{d\left(T_g/T\right)}\right|_{T=T_g} \qquad \left(0 \le T_g/T \le 1\right). \tag{4.57}$$

Equation (4.57) provides a mathematically direct derivation of m_{min} by simply demanding that the derivative in eq. (4.57) be independent of temperature for $0 < T_g/T < 1$.

Angell [CAAP] has described how certain features of fragility can predict some "universal" features of the WLF constants. In particular for T* = Tg the value mmin = 16 immediately given

The thermodynamic and kinetic definitions of fragility are equivalent if the Adam-Gibbs (AG) [18] model for liquid state transport properties is accepted. This model gives rise to equations that are almost indistinguishable from the Fulcher equation in most cases and for the hyperbolic form of $\Delta C_p\left(T\right)=C/T$ it reproduces the Fulcher equation exactly. The ease with which this equation can be extended through the glass transition to the glassy state was quickly recognized by Macedo and Napolitano [19], Goldstein [20], Kovacs et al. [21], Plazek and Magill [22,23] and Howell et al. [24], but was not used explicitly for enthalpy relaxation until the pioneering work of Scherer [25] and in later studies by Hodge [26].

The AG model is based on transition state theory and the hypothesis that a temperature dependent number of moieties needs to rearrange cooperatively for relaxation to occur. The transition state activation energy E_A is then given by

$$E_A = z\Delta\mu \tag{4.58}$$

where $\Delta\mu$ is an elementary excitation energy per moiety and z is the number of moieties that cooperatively rearrange. The linear addition of $\Delta\mu$ for each moiety implicitly assumes that the moieties do not interact and this has been challenged by Ngai et al. who have proposed an alternative "coupling model" [27]. Only the minimum value z^* of z significantly contributes to the relaxation time [18] and its value is assumed to be a function of temperature derived by simplistically equating two expressions for the configurational entropy per moiety

$$\frac{S_c\left(T\right)}{N_A}=\frac{s_c^*}{z^*\left(T\right)}, \tag{4.59}$$

where $S_c\left(T\right)$ is the macroscopic configurational entropy (defined below), N_A is Avogadro's number, and s_c^* is the configurational entropy associated with the smallest number of particles capable of rearranging that is often taken to be $k_B \ln 2$ (two configurations, one before and one after rearrangement). The result that configurational entropy is the fundamental property that determines the rate of relaxation is plausible because if more configurations are available then relaxation can be expected to be faster. Explicitly

$$\tau_0 = A\exp\left(\frac{E_A}{RT}\right)=A_{AG}\exp\left(\frac{z^*\left(T\right)\Delta\mu}{k_BT}\right)=A_{AG}\exp\left(\frac{N_A s_c^*\Delta\mu}{k_BTS_c\left(T\right)}\right) \tag{4.60}$$

where a pre-exponential factor $\left[1-\exp\left(-\Delta\mu/k_BT\right)\right]^{-1}$ has been equated to unity because typically $\Delta\mu >> k_BT$.

The quantity $S_c(T)$ is given by

$$S_c(T) = \int_{T_2}^{T} \frac{\Delta C_p(T')}{T'} dT' = \int_{\ln T_2}^{\ln T} \Delta C_p(T') d\ln T' \tag{4.61}$$

where T_2 is the temperature at which $S_c(T)$ extrapolates to zero (denoted as such to emphasize that it is an adjustable nonlinear kinetic parameter rather than the Fulcher T_0 for $T > T_g$ or the thermodynamic Kauzmann temperature T_K discussed below). Assessment of $\Delta C_p(T)$ is not trivial. It must be obtained by extrapolations that are necessarily uncertain in part because the glassy heat capacity $C_{pg}(T)$ must be obtained at temperatures well below T_g to ensure that relaxation effects are not included in its temperature dependence so that long extrapolations are required. Huang and Gupta [28] have evaluated expressions for $C_{pg}(T)$ suitable for extrapolation into and above the glass transition temperature range for a soda lime silicate glass. The uncertainty in $\Delta C_p(T_g)$ also depends on the uncertainty in the extrapolated C_{pl} that is however much smaller than that in $C_{pg}(T_g)$. It is common to assume that $\Delta C_p(T_g)$ is totally configurational but this has been challenged by Goldstein [29,30] who has argued that it may contain significant contributions from vibrational and secondary relaxation sources. It is however possible that such non-configurational contributions to $\Delta C_p(T)$ could also contribute to "S_c" in the AG model so that using $\Delta C_p(T)$ regardless of its origin could still be valid. The debate about the configurational contribution to $\Delta C_P(T)$ is therefore probably not resolvable because of all the unknown factors that determine structural relaxation. The default position is that all the contributions to $\Delta C_p(T_g)$ whatever they may be all important determine structural relaxation.

The AG function for $\tau_0(T)$ depends on the functional form of $\Delta C_p(T)$. For

$$\Delta C_p = C = \text{constant} \tag{4.62}$$

the "AGL" function for the structural relaxation time is

$$\tau_0(T) = A_{AGL} \exp\left[\frac{B_{AGL}}{T \ln(T/T_2)}\right] \tag{4.63}$$

where

$$B_{AGL} = \frac{N_A s_c^* \Delta\mu}{k_B C}. \tag{4.64}$$

Equation (4.63) is almost indistinguishable from the Fulcher equation and in fact retaining only the first term in the expansion of the logarithmic term reproduces the Fulcher form. The expression

$$\Delta C_p(T) = C' T_g / T \tag{4.65}$$

implies

$$S_c(T) = \Delta C(T_g) T_g [1 - T_2/T] / T_2 \tag{4.66}$$

so that

$$\tau_0\left(T\right) = A_F \exp\left[\frac{B_F}{T\left(1 - T_2/T\right)}\right], \tag{4.67}$$

i.e. the Fulcher form is predicted with

$$B_F = \frac{N_A s_c^* \Delta\mu T_2}{k_B T_g \Delta C_p\left(T_g\right)}. \tag{4.68}$$

As noted in [8] eq. (4.65) has a stronger temperature dependence than that observed for most polymers, according to plots of the data compiled in Ref. [31]. Since eqs (4.63) and (4.67) are almost indistinguishable the AG model can accommodate most approximations to the Fulcher equation that are found experimentally [32,33].

Equations (4.60) and (4.66) imply that z^* is proportional to $1/\left(1 - T_2/T\right)$. Thus z^* and the barrier height $z^*\Delta\mu$ diverge as $T \rightarrow T_2$ and simplistically this divergence can be expected to prevent T_g approaching T_2 [26,34]. Since z^* is conceivably associated with some form of correlation length it is of interest that the correlation length computed from a random field Ising model also diverges as $\left(1 - T_c/T\right)^{-\gamma}$ [35] although no evidence for a correlation length was observed in a viscosity study of glycerol by Dixon et al. [36] nor in a molecular dynamics simulation by Ernst et al. [37]. On the other hand if z^* is interpreted in dynamic terms, for example as the minimum number of particles needed for the ensemble averaged time correlation function to be independent of size, it would not necessarily be seen structurally. It is also possible that z^* corresponds in some way to the "dynamic characteristic length" defined by the ratio of the frequency of the Raman "boson" peak to the speed of sound [38,39]. Adam-Gibbs behavior has been observed in a spin facilitated kinetic Ising model described by Frederickson [40] and as noted above the AG equation has also been extended through the glass transition to the glassy state (discussed in detail in §4.8.3).

The claim made above that the kinetic and thermodynamic definitions of fragility can be made physically consistent by the AG model can now be explained. Since S_c is more strongly temperature dependent for greater $\Delta C_p(T_g)$ (greater thermodynamic fragility) eq. (4.60) indicates that the structural relaxation time has a more non-Arrhenius temperature dependence and larger m [eq. (4.55)] (greater kinetic fragility).

4.8.2 Glassy State Relaxation

Because glasses are usually in a non-equilibrium state they can isothermally relax towards the equilibrium state. A discussion of this phenomenon has been given by Hodge [8,39]. There are two essential aspects of glassy state relaxation kinetics – nonexponentiality and nonlinearity. The former is a characteristic of relaxation in essentially all condensed media (water is an exception as usual) and has been discussed extensively in Chapter 1. Nonlinearity is absent for most electrical relaxation phenomena (Chapter 2) and becomes important for viscoelastic relaxation only for high stresses and strains – linear viscoelastic relaxation is still applicable for practically significant stresses and strains (Chapter 3). But for structural relaxation nonlinearity is fundamental – it cannot be ignored for even small perturbations and is responsible for several observed phenomena such as glassy state relaxation occurring on human lifetime scales rather on inhuman scales of centuries or longer [41]. Experimental evidence for nonlinearity in glassy state relaxation is exemplified by the creep data of Struik [42] that are reproduced in [41]. Creep is essentially a quantitative measure of the fractional increase in length with time of a vertically suspended small diameter thread of material that has a hanging weight on it (Chapter 3). These data were recorded for time intervals that were about 10% of the annealing times t_a. The creep curves move to longer times with increasing t_a but the shape of each creep curve is essentially the same for all t_a - thus the characteristic relaxation time increases with t_a. A generally excellent description of the increase in relaxation time τ_0 with t_a is given by the Struik relation

$$\tau_0 = K t_a^{\mu} \tag{4.69}$$

where K is independent of time but dependent on temperature and material. The quantity $\mu \le 1$ is an empirical "nonlinearity" parameter referred to here as the Struik shift parameter that is often independent of time but dependent on annealing temperature. The nonlinearity of relaxation expressions that invoke eq. (4.69) is eliminated by the reduced time defined by [43,44]

$$\xi(t) \equiv \int_{-\infty}^{t} \frac{dt'}{\tau(t')} \tag{4.70}$$

so that for $\tau(t') = \tau_0^{1-\mu} t'^{\mu}_{a}$ $\left[\xi(-\infty) = 0\right]$

$$\xi(t) = \frac{(t/\tau_0)^{(1-\mu)}}{(1-\mu)}. \tag{4.71}$$

For the WW function [8]

$$\exp\left\{-\left[\xi(t)\right]^{\beta}\right\} = \exp\left\{-\left[\frac{(t/\tau_0)^{(1-\mu)}}{(1-\mu)}\right]^{\beta}\right\} = \exp\left\{-\left[\frac{t^{(1-\mu)\beta}}{(1-\mu)\tau_0^{1-\mu}}\right]\right\} = \exp\left[-\left(\frac{t}{\tau_0'}\right)^{\beta'}\right] \tag{4.72}$$

where

$$\beta' = 1-\beta \tag{4.73}$$

and

$$\tau_0' = \tau_0 (1-\mu)^{1/(1-\mu)}. \tag{4.74}$$

Equation (4.74) corrects eq. (35) in ref [8]. The mathematical equivalence of the linear and nonlinear WW equations exhibited in eq. (4.72) has engendered many published analyses that are physically unreasonable because in the name of "simplicity" they invoke the linear WW equation in situations that demand the consideration of nonlinearity, such as glassy state relaxation for which the Struik relation eq. (4.69) was originally observed experimentally. Some of these incorrect analyses are cited as refs. 53-60 in [8].

Another widely used metric for nonlinearity is the fictive temperature T_f introduced by Tool [45-47], originally in an oral presentation in 1924. Thus nonlinearity was recognized as being important to structural relaxation well before nonexponentiality was. Ironically Tool's analysis was for silicate glasses that are now known to have some of the least nonlinear structural relaxation kinetics. Qualitatively T_f is the temperature at which some non-equilibrium property (volume, enthalpy, entropy, relative permittivity, etc.) of a material would be the equilibrium one, and is typically different for different properties of the same material in the same state. For enthalpy *H*, whose relaxation phenomenology is representative of all properties, T_f is defined by

$$H(T) = H_e(T_f) - \int_T^{T_f} C_{pg}(T')\,dT' \qquad (4.75)$$

where $H_e(T_f)$ is the equilibrium value of *H* at T_f and $C_{pg}(T')$ is the temperature dependent isobaric heat capacity of the glass. Equation (4.75) is illustrated in [8] and its temperature derivative is (using eq. 1.18)

$$\frac{dT_f}{dT} = \frac{\left(C_p - C_{pg}\right)\Big|_T}{\left(C_{pe} - C_{pg}\right)\Big|_{T_f}} \approx \frac{\left(C_p - C_{pg}\right)\Big|_T}{\left(C_{pe} - C_{pg}\right)\Big|_T} \equiv C_p^N \qquad (4.76)$$

where C_{pe} is the equilibrium (liquid or rubber) isobaric heat capacity and C_p^N is the normalized heat capacity. It is usually assumed that $dT_f / dT = C_p^N$ but this is probably unjustified in general [48,49(Sindee Simon)].

Applying mechanical stresses (both shear and tensile) or hydrostatic pressure to, or inducing swelling by vapor absorption rapid desorption in, polymers all decrease the average isothermal structural relaxation time in the glasses. Representative but not comprehensive accounts of these effects are given in [8,50,51] that include many references to original publications on the effects of nonthermal perturbations on enthalpy relaxation in particular. Applications of the TNM phenomenology to these histories [50] usually approximate applied stresses and pressure as instantaneous isothermal changes in fictive temperature. An instructive example is the formation of "pressure densified polystyrene" by cooling the sample through the glass transition temperature range under hydrostatic pressure and then releasing the pressure in the glassy state (typically at room temperature). The resultant glass has a higher density and enthalpy than that prepared by cooling under ambient pressure and has more rapid annealing kinetics (shorter structural relaxation time). The fact that relaxation is faster at a smaller volume is inconsistent with free volume models frequently used by polymer physicists [52] but is consistent with enthalpy/entropy models such Adam-Gibbs.

4.8.3 The Glass Transition

4.8.3.1 Introduction

This vast subject is the focus of two excellent books by Donth [53,54] and at least three reviews [7,8,41], and its applications to material science have been well described by Scherer [55]. This section only considers the relaxation aspects of the glass transition phenomenon in detail, but a brief general overview of it is nonetheless given to provide a context for the relaxation phenomenology. In particular the intricate and still debated link between thermodynamics and kinetics for the observed glass transition phenomenon is discussed.

The glass transition is not understood at a fundamental level. Nobel laureate Philip Anderson stated in *Science* [56], when asked at the end of the 20th century about the most important challenges awaiting 21st century science he answered "The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. …". Earlier he stated in *Physics Today* (1991) "… Glass itself remains one of the deepest puzzles in all of physics." This author's opinion is that new mathematics will be required before this puzzle is solved.

4.8.3.2 "Glass Transition Temperature" T_g

The phrase "glass transition temperature" is a misnomer because, as noted above (§4.8.1) the transition from a liquid (relaxation time << observation time) to a glass (relaxation time >> observation time) during cooling and heating occurs over a range of temperature. The essential reason for confusion about "T_g" is that the "glass transition" is not a transition in the traditional sense but rather a phenomenon that occurs over an unexpected and thus far theoretically unexplained relatively narrow temperature range. An excellent account of the physics of the glass transition as a condensed matter phenomenon is given in Angell's review article [7]. Nonetheless an ASTM publication [57] compiles several contributions to a session on definitions of the glass transition temperature of which the contribution by Moynihan [58] is most relevant here. The ASTM specification for T_g by DSC is published at www.astm.org/Standards/E1356.htm.

There are three basic definitions of a DSC "T_g" that are in common use, all of which should (but not often enough) include a specification of scan rates (cooling and heating). Cooling rate is more important but for glasses formed at unknown cooling rates or by vapor deposition or other nonthermal processes only the heating rate is known, but it should still be specified. The three definitions are:

(a) *Midpoint*. The center of the transition range (often recorded by DSC).

(b) *Onset*. The temperature at which departure from the glassy heat capacity first occurs in a DSC heating scan. It is often determined by drawing a tangent line through the point of inflection of $C_p(T)$ and taking T_g to be the temperature at which this line intersects the extrapolated glassy heat capacity. It typically corresponds to the temperature at which the excess heat capacity over that of $C_{pg}\left(T\right)$ is 5 – 10% of $\Delta C_p(T_g)$.

(c) *Glassy Fictive Temperature* (no annealing). Computed from integration of the heat capacity. This is the best definition but also the least convenient. It usually has a similar value to the onset definition if the heating and cooling rates are similar.

As noted the first two definitions apply to both cooling and heating but values from cooling data are preferred. The reason for preferring cooling is that heat capacity overshoots and a strong dependence on the TNM parameters x and β make the heating data more dependent on material and thermal history [8].

As illustration of these issues consider the question "what is 'T_g' for an annealed glass compared with a non-annealed glass?" As just noted the best definition of "T_g" is the glassy state value of the fictive temperature T_f' (also see below), that decreases with slower cooling rate for unannealed glasses as well as for longer annealed times. However upon reheating enthalpy recovery then occurs at higher temperatures because of nonlinearity – lower glassy fictive temperatures lengthen the starting average relaxation time so that higher temperatures must be reached before the average relaxation time becomes short enough for relaxation back to equilibrium to occur. The heat capacity increase from glassy values to liquid values upon heating therefore begins at a higher temperature and the midpoint definition of T_g also increases.

The debate about "what is T_g" that has been discussed above is however not of great importance to the detailed kinetics of structural relaxation because the temperature dependencies of structural relaxation times scale with T_g and the glass transition temperature range simply shifts along the temperature axis. However it is of interest to discuss the value of "T_g" in one case because it illustrates yet again the flexibility of WW-type functions. For binary mixtures of materials with very different values of T_g (polymer/solvent mixtures for example) the dependence of T_g on the concentration c of the lower T_g component is often well described by

$$T_g\left(c\right)=T_g^0\exp\left[-\left(kc\right)^\beta\right] \tag{4.77}$$

where T_g^0 is the higher value of T_g and k and β are empirical constants. Equation (4.77) was discovered and used by the present author in 1989 [59] without knowledge of papers by Phillies et al. the first of which was published in 1985 [60]. The latter paper also discussed power laws for molecular weight and probe radius for light scattering that are subsumed into k in eq. (4.77).

4.8.3.3 Thermodynamic Aspects of the Glass Transition

The isobaric heat capacity of a supercooled liquid exceeds that of the crystal at the same temperature so that the excess entropy of a liquid over that of the crystal decreases with decreasing temperature. Extrapolations for many materials suggest that this excess entropy would vanish (or nearly so) at a temperature well above absolute zero. At this temperature the entropy of the supercooled liquid approaches that of the crystal and if the same trend were to extend down to absolute zero the entropy of the liquid would be less than that of the crystal, in conflict with the third law of thermodynamics. This difficulty was first recognized by Kauzmann [61] and the extrapolated temperature at which the supercooled liquid and crystal entropies become equal is known as the Kauzmann temperature T_K. The extrapolation is often referred to as the Kauzmann "paradox" because it seems paradoxical that the intervention of a kinetic event, the observed glass transition, averts rather than resolves a thermodynamic impossibility. The value of T_K is calculated by equating the excess entropy of the liquid over that of the crystal to the entropy of melting ΔS_m

$$\Delta S_m = \int_{T_K}^{T_m} \left(\frac{\left[C_{pl} - C_{pg} \right](T)}{T} \right) dT \, , \tag{4.78}$$

where T_m is the melting temperature. The uncertainty in T_K is unusually large in part because $\Delta C_p(T)$ is obtained by extrapolation and in part because of possible different crystal forms with different values of T_m and ΔS_m. For polymers the uncertainty is even larger because of the need to correct for tacticity and partial crystallinity. As noted above (§4.8.2) Goldstein [29,30] has argued that $\Delta C_p(T)$ is probably not entirely configurational and may contain significant contributions from vibrational and secondary relaxation sources. He estimated that between 20 and 80% of $\Delta C_p(T)$ could originate from non-configurational sources and noted that this renders even more uncertain the extrapolations required to assess T_K. Nonetheless calculated values of T_K are always found to be less than T_g although in some cases the difference can be as small as 20 K [62,63]. The value of T_K is often close to T_0 of the VTF equation [64] suggesting again that the kinetic and thermodynamic aspects of the glass transition may be related.

Three resolutions of the thermodynamic difficulties imposed by $T_K > 0$ have been suggested. One is that the extrapolation of excess entropy to low temperatures has no firm basis and that the prediction $T_K > 0$ is a spurious result of inappropriate extrapolation [65,66]. As noted already, however, the extrapolation is only 20 K or so for some materials and a non-zero T_K seems inescapable in these cases. A second resolution, suggested by Kauzmann [61], is that the extrapolation is irrelevant because the thermodynamic driving force for crystallization would always intervene before the entropy problem manifested itself. However this intervention has been shown to be extremely unlikely in some systems [67], and it may actually be impossible in two bizarre systems (CrO_3-H_2O [68] and RbAc–H_20 [69]) for which T_g exceeds the (extrapolated) eutectic temperature (the Kauzmann analysis can be applied to eutectic mixtures [67]). The third resolution is that an Ehrenfest second-order transition occurs at T_K at which $\Delta C_P(T)$ falls rapidly (simplistically instantaneously) to zero similar to that which is observed kinetically at T_g. The Ehrenfest second-order transition temperature T_K is of course unobservable because of kinetic factors. It is difficult to refute this hypothesis other than to dismiss it as an artifact of extrapolation but as has just been noted this objection is itself weakened by the fact that very short extrapolations are needed in many cases. Furthermore an entropically based second-order transition at T_K has been derived for polymers by Gibbs and DiMarzio [70], and although this theory has been criticized [71] its predictions agree well with experimental observations near T_g, including those on the effect of molecular weight on T_g for polymeric rings [72,73]. There are also several two state models ([74,75] for example) that predict that $\Delta C_p(T)$ passes through a maximum at $T_{\max}$ which is necessarily below T_g because such a maximum has never been observed. If these models accommodate sharp decreases in $\Delta C_p(T)$ below $T_{\max}$ then they could essentially resolve the Kauzmann "paradox" without invoking an ideal Ehrenfest second order transition. For example a heat capacity function that mirrors the Debye dielectric loss function

$$\Delta C_p\left(T\right)=\frac{C\Omega T}{1+\Omega^2 T^2} \tag{4.79}$$

where C is a constant and $T_{\max}=1/\Omega$ has a maximum and a sharp decrease for $T<T_{\max}$. Note that for $T >> T_{\max}$ eq. (4.79) yields $C_p(T) \propto 1/T$ that is often approximately observed and that as T approaches $T_{\max}$ from above the T dependence becomes weaker than $1/T$, as observed for most polymers [31]. Preliminary results [76] indicate that a good fit (<10%) to the Fulcher equation is obtained from the heat capacity function given by eq. (4.79) for the temperature range T_g to $1.5T_g$ with a T_0 value almost three times less than $T_{\max}$ [76]. Other preliminary calculations using a combination of two halves of such "Debye loss" functions in which eq. (4.79) describes C_p for $T > T_{\max} = 1/\Omega$ and a narrower version [76]

$$\Delta C_p\left(T\right)=\frac{C\left(\Omega T\right)^f}{1+\left(\Omega T\right)^{2f}}. \tag{4.80}$$

describes C_p for $T < T_{\max}$ with $f > 1$ with about equal accuracy. Larger values of f produce sharper low frequency decreases in $C_p(T)$ and in the limit $f \to \infty$ $C_p(T)$ approaches the instantaneous decrease approximation. Although as just noted these heat capacity functions do not (surprisingly) produce better fits to the Fulcher equation than eq. (4.79) the best fit values of T_0 more closely approach the temperature $T_{1/2} < T_{\max}$ at which ΔC_p is half the maximum. Preliminary analyses also suggest that the ratio $R = T_0/T_{1/2}$ is approximately given as a function of f by

$$\left(R-1\right)\approx 0.64\exp\left[-2.33\left(f-1\right)\right]. \tag{4.81}$$

Angell [77] describes proposed modifications to the Kauzmann analysis that suggest that a first order transition, rather than an Ehrenfest second order transition, occurs at the low temperature limit of a supercooled liquid. However true this may be it does not change the Adam-Gibbs model for relaxation times because it only affects the calculation of "T_K" and does not affect $S_c(T,T_f)$ apart from its behavior when it approaches zero, and the latter does not affect the physics of the Adam-Gibbs model near T_g. This subject is discussed in detail in [76] where it is argued that whether S_c has a sharp change in slope when it approaches zero at T_K (2nd order transition) or a discontinuous step to zero at some $T_1 > T_K$ (1st order transition) only changes the empirical SH parameter T_2 and not the physical basis of the Adam-Gibbs model. In view of the possibility that $T_2 \approx T_1 > T_K$ the experimental SH parameter T_2 might be expected to exceed T_K more often than not. It is also possible that any difference between T_1 and T_2 is less than the experimental uncertainty in T_2. In any case the values of T_K, T_0 (Fulcher) and T_2 (SH) often agree within uncertainties (that are too rarely stated but can reasonably be assumed to be about ±20 K if they are not) and when they do not agree it is always found that they are all less than T_g. For T_2

the latter is indicated by the fact that observed TNM x parameters are always positive and less than unity [eq. (4.88)], apart from a few possible cases where the data analyses are suspect. The fundamental uncertainty about whether T_1 or T_K is the low temperature limit of the liquid state is analogous to the fundamental uncertainty about and probable irrelevance of the contributions to $\Delta C_p\left(T_g\right)$ - whether they are configurational, vibrational or secondary (§4.8.1).

The Kauzmann analysis is not the only factor that suggests a thermodynamic dimension to the glass transition - two other observations also support it:

(a) Glassy state relaxation data indicate that not only the creep data shown in [41] but also relaxation data for thermodynamic properties such as volume and enthalpy also shift to longer time scales with annealing. As noted in [41] this implies a link between the thermodynamic and nonlinear kinetic aspects of glassy state relaxation.

(b) There is compelling circumstantial evidence that for two component mixtures that are predicted or inferred to have an upper consulate phase separation temperature the glass transition temperature over the composition range of phase separation is nearly independent of composition [78] and references therein). This near constancy of T_g with composition corresponds to the near constancy of the chemical potential of each component and a link between thermodynamics and kinetics seems inescapable in these cases.

4.8.3.4 Kinetics of the Glass Transition

The mathematical description of these kinetics must necessarily incorporate those of the supercooled liquid state (§4.8.2) and the glassy state (§4.8.3) as limiting cases. We describe here just those formalisms that invoke the equilibrium temperature T and the fictive temperature T_f – others such as the KAHR description are discussed in [8]. There are two expressions for $\tau_0\left(T,T_f\right)$ in common use. The Tool-Narayanaswamy-Moynihan (TNM) expression [79] is a generalization of the Arrhenius equation:

$$\tau_0\left(T,T_f\right)=A_{TNM}\exp\left[\frac{xh}{RT}+\frac{(1-x)h}{RT_f}\right] \qquad \left(0<x\le 1\right). \tag{4.82}$$

The NLAG ("Nonlinear Adam-Gibbs") [26] expression is obtained from the AG equation (4.60) by assuming that S_c is a function of T_f rather than of T:

$$S_C\left(T_f\right)=C\left(1-T_2/T_f\right) \tag{4.83}$$

so that

$$\tau_0\left(T,T_f\right)=A_{SH}\exp\left[\frac{B_{SH}}{T\left(1-T_2/T_f\right)}\right]. \tag{4.84}$$

Equation (4.84) has been called by several names: Adam-Gibbs-Vogel (AGV), Adam-Gibbs-Fulcher (AGF), Nonlinear Adam-Gibbs (NLAG) [26] and Scherer-Hodge (SH) [25,26]. The last name is not this author's choice but is increasingly common and so is used here. The full and partial temperature derivatives of eq. (4.84) are

$$\frac{d\ln\tau_0\left(T\right)}{d\left(1/T\right)}=\frac{B_{SH}}{\left(1-T_2/T\right)^2}=\frac{h}{R} \tag{4.85}$$

and

$$\left[\frac{\partial\ln\tau_0\left(T\right)}{\partial\left(1/T\right)}\right]_{T_f}=\frac{B_{SH}}{\left(1-T_2/T_f\right)}=\frac{xh}{R}. \tag{4.86}$$

Applying eqs. (4.85) and (4.86) to the glass transition temperature range where the approximation $T\approx T_f\approx T_g$ is appropriate reveals that the TNM and SH parameters are related as [8, 26]

$$x\approx 1-T_2/T_g; \tag{4.87}$$

$$T_2=T_g\left(1-x\right) \tag{4.88}$$

and

$$B_{SH}\approx x^2h/R\approx\left(1-T_2/T_g\right)^2 h/R; \tag{4.89}$$

$$\frac{h}{R}=\frac{B_{SH}}{\left(1-T_2/T_g\right)^2}, \tag{4.90}$$

where T_g now refers particularly to the onset definition that is closer to the glassy state. Equation (4.90) is a generalization of eq. **Error! Reference source not found.** that applies to the nonequilibrium glass transition temperature range. Equations (4.87) - (4.90) have proven to be good approximations.

A more general AG expression for the TNM nonlinearity parameter x in terms of $\Delta C_p(T_g)$ and the residual configurational entropy $S_c(T_g)$ [8] is

$$x_{AG}\approx\frac{S_c\left(glass\right)}{S_c\left(glass\right)+\Delta C_p\left(T_g\right)} \tag{4.91}$$

where again T_g refers to the onset definition. Equation (4.91) predicts lower values of x for larger values of $\Delta C_p(T_g)$ and smaller values of $S_c(glass)$. Note that for larger $\Delta C_p(T_g)$ more entropy is lost over the glass transition range (assuming the width of the glass transition does not change substantially) so that $S_c(glass)$ is smaller if $\Delta C_p(T_g)$ is larger.

The relationship between the TNM nonlinearity parameter x and the Struik shift parameter μ is not simple. Essentially the Struik relation is a special case of TNM. A simplified analysis for restricted thermal histories has been given for pharmaceutical glasses [80] in which it was noted that the values of μ depend on both the annealing temperature T_a and the WW nonexponentiality parameter β as well as on x.

The nonlinearity parameter x has been shown to be inversely related to the Angell fragility parameter m for the Scherer-Hodge (nonlinear Fulcher) equation [8,17,26]. Since the SH equation is usually a good description of $\ln\tau_0\left(T,T_f\right)$ a generally inverse relation between x and m seems more probable although a rigorous mathematical derivation is not yet at hand. Here a more general analysis than SH is given that establishes some specific conditions required for an inverse relation between x and m to hold and contains the SH result as a special case. For convenience the general form

$$\tau_0\left(T,T_f\right)=A_{mx}\exp\left[f\left(T\right)g\left(T_f\right)\right] \qquad (4.92)$$

is assumed that apart from the separation of variables is the most general function possible. The fragility index *m* given by eq. (4.55) is for eq. (4.92) (when $T_f = T$)

$$m=\left[\frac{1}{RT_g\ln(10)}\right]\left\{f\left(T\right)\left[dg\left(T\right)/d\left(1/T\right)\right]+g\left(T\right)\left[df\left(T\right)/d\left(1/T\right)\right]\right\}. \qquad (4.93)$$

Full and partial differentiation of eq. (4.93) with respect to 1/*T* yields

$$\frac{h}{R}=\frac{d\ln\tau_0\left(T_f=T,T\right)}{d\left(1/T\right)}=g\left(T\right)\frac{df}{d\left(1/T\right)}+f\left(T\right)\frac{dg}{d\left(1/T\right)}\Bigg|_{T=T_g}; \qquad (4.94)$$

and

$$\frac{xh}{R}=\frac{\partial\ln\tau_0\left(T_f,T\right)}{\partial\left(1/T\right)}\Bigg|_{T=T_f=T_g}=g\left(T_g\right)\frac{df}{d\left(1/T\right)}\Bigg|_{T=T_g} \qquad (4.95)$$

so that

$$\frac{1}{x}=\frac{g\dfrac{df}{d\left(1/T\right)}+f\dfrac{dg}{d\left(1/T\right)}}{g\dfrac{df}{d\left(1/T\right)}}\Bigg|_{T=T_f=T_g}=\left[1+\frac{d\ln g/d\left(1/T\right)}{d\ln f/d\left(1/T\right)}\right]\Bigg|_{T=T_f+T_g} \qquad (4.96)$$

Equations (4.93) and (4.96) yield

$$x^{-1}=\frac{mRT_g\ln\left(10\right)}{g\,df/d\left(1/T\right)}\Bigg|_{T=T_f=T_g}. \qquad (4.97)$$

The function $df/d\left(1/T\right)\big|_{T_g}$ must be approximately equal to *xh*/*R* to ensure that the experimentally observed Arrhenius behavior in the glassy state is reproduced so that

$$\frac{mR^2T_g\ln\left(10\right)}{hg\left(T_g\right)}\approx 1. \qquad (4.98)$$

The relationship between *x* and *m* therefore depends on the *x*-dependence of $g(T_f = T_g)$. For the SH expression $g\left(T_g\right)=\left(1-T_2/T_g\right)^{-1}\approx x^{-1}$ and *m* is indeed inversely proportional to *x*.

4.8.3.5 Thermorheological Complexity (TRC)

All the analyses discussed so far consider the TNM and SH parameters to be constant and therefore independent of temperature. However there are several reports scattered throughout the literature that some of these parameters may be temperature dependent, in particular that the distribution of relaxation times may depend on both *T* and T_f. The following discussion of this possibility draws heavily on [81] - in particular the consequences of a distribution of activation energies (in both TNM and SH formalisms) are explored.

Consider first an Arrhenius temperature dependence for the structural relaxation time τ_i corresponding to the component E_i of a distribution of activation energies

$$\ln \tau_i = \ln A_A + \frac{E_i}{RT}. \tag{4.99}$$

For a Gaussian distribution of activation energies with standard deviation σ_E the standard deviation $\sigma_{\ln\tau}$ in the corresponding logarithmic Gaussian distribution of relaxation times $g(\ln \tau)$ is

$$\sigma_{\ln \tau} = \frac{\sigma_E}{RT}. \tag{4.100}$$

Thus any measured distribution of relaxation times is temperature dependent if there is an underlying distribution of activation energies. Since any physically reasonable distribution of activation energies is unlikely to be a delta function for condensed media thermorheological simplicity must be regarded as an approximation whose accuracy can only be assessed if experimental uncertainties are known. The latter are unfortunately not even estimated for the vast majority of reports in the materials science literature. For nonlinear expressions of relaxation times the distribution of $\ln(\tau)$ is a function of both T_f as well as T. For example the SH expression (eq. (4.84)) yields (for a Gaussian distribution in B)

$$\sigma_{\ln \tau} = \frac{\sigma_B}{T\left(1 - T_2 / T_f\right)}. \tag{4.101}$$

The Gaussian standard deviations cited above have their counterparts in the widths of other distributions such as WW so that eqs. (4.100) and (4.101) are therefore generally applicable.

Implementation of TRC phenomenologies requires that the decay function be expressed as a Prony series with coefficients g_i that are T and T_f dependent [81]. For the WW decay function for example

$$\exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right] = \sum_{i=1}^{N} g_i\left(T, T_f\right) \exp\left[-\left(\frac{t}{\tau_i}\right)\right] \tag{4.102}$$

where the best fit values of both N and g_i depend on β. This is time consuming because the coefficients g_i must be re-calculated at every temperature step although good approximations that do so every $n > 1$ steps may be possible. Estimates by the present author suggest that computation times are probably a daunting $10^{0\pm1}$ days, depending on $\beta(T_g)$.

4.9 Experimental DSC Results

4.9.1 Data Analysis

The DSC technique is not strictly calorimetry but the name is embedded in the literature and changing it here would serve no useful purpose. The technique measures heat capacity by recording the heat flow into a sample needed to maintain a programmed temperature during cooling and reheating through the glass transition temperature range. It is described in modest detail here because enthalpy relaxation is a good surrogate for structural relaxation in general and there are abundant experimental DSC data available for analysis because the technique is so experimentally convenient. Modifications of the technique such as modulated DSC (MDSC) are not discussed apart from noting that an early version of a MDSC instrument (1994) using a temperature modulation of amplitude 1^{o}C and frequency 0.017 Hz produced different heats of melting than the same instrument in its DSC mode for a series of five two-component mixtures

[82] – MDSC heats of melting were 1.4 ± 0.3 times larger than the DSC values.

The term "differential" originates from the fact that the difference in heat inputs to two separate instrument pans (sample and reference) is measured in order that the sample and reference are at the same temperature during heating and cooling. Heat input into the reference pan is adjusted to maintain the specified rate of change of temperature – for cooling this requires a cold bath (typically ice/water, dry ice or liquid nitrogen) in thermal contact with the reference pan (for liquid nitrogen coolant helium is needed as a carrier gas because nitrogen would obviously condense). The heat capacity is then computed from

$$C_p(T) = \left(\frac{dq}{dt}\right) \bigg/ \left(\frac{dT}{dt}\right) = \left(\frac{dq}{dt}\right) \bigg/ Q_{c,h} \qquad (4.103)$$

where $Q_{c,h}$ is the cooling/heating rate (not a good nomenclature but it is entrenched) and dq/dt is the measured differential heat input (typically given in mW). Note that for any given C_p the differential heat input is proportional to $Q_{c,h}$ so that there is a lower limit to $Q_{c,h}$ that is determined by instrumental sensitivity.

Thermal lag shifts the DSC temperature calibration by an amount $\tau_{th}Q_h$ ([83] and references therein). This is the basis of temperature calibration that usually uses the melting temperature of a standard material (often indium) and preferably of two (the second is often zinc). However the value of τ_{th} for pure metals is undoubtedly smaller than for most amorphous materials, especially polymers, because of the large thermal conductivity of metals compared with other materials. Hodge and Heslin [83] reported a value of 5 ± 0.5 s obtained from indium temperature calibration compared with 15-17 s for their polymer sample. This discrepancy is atypically large because the sample shape was deliberately irregular in order to maximize heat transfer effects but it does illustrate uncertainties in temperature calibration.

Sample preparation is straight forward and experimental reproducibility is generally excellent for inorganic and simple organic glasses. Polymers present several complications of which sample reproducibility is probably the most important. Variables such as molecular weight, molecular weight distribution and degree of crystallinity are too often not reported or are implicit in the identification of the manufacturer and/or product name. Also crystallinity and crystal morphology can be affected by thermal histories before a DSC run – for example the temperature and time spent above T_g for stabilization. Even when these are stated it is difficult to quantify any material changes, particularly in crystallinity or crystal morphology. For example changes in the micro crystallinity of PVC with the temperature excursions required to make the traditional sample disk that were employed by Pappin et al. [84] were almost certainly the cause of their TNM parameters being significantly different [8] from those found by Hodge and Berens [81] who used the original powdered PVC material that was sent to the authors of [84].

The reproduction of the heat capacity change over the glass transition temperature range during constant cooling and heating rates is a good test of the TNM formalism and passes with flying colors, as has been shown by Moynihan et al.. Hodge and Berens later introduced annealing times into the Moynihan calculations [85]. All these calculations combine the TNM expression eq. (4.82) or SH expression eq. (4.84), the reduced time eq. (4.70), and Boltzmann superposition (Chapter One) and these calculations are discussed in detail here because they illustrate many aspects of structural relaxation kinetics and also because they provide many insights into the glass transition phenomenon. Details of the data analysis are described in [8,83,85] and references therein.

During DSC scanning both T and T_f change with time (for isothermal annealing only T_f changes of course). Thus the reduced time eq. (4.70) can be expressed in terms of the TNM eq. (4.82) or SH eq. (4.84) using time dependent T and T_f:

$$\tau_0(t) = A_{TNM} \exp\left[\frac{xh}{RT(t)} + \frac{(1-x)}{RT_f(t)}\right] = A_{SH} \exp\left[\frac{B_{SH}}{T(t)\left[1-T_2/T_f(t)\right]}\right]. \qquad (4.104)$$

This is the first step in computing $T_f[T(t)]$ and thence $C_p^N(T) \approx dT_f/dT$. The second step is to use Boltzmann superposition by representing rate cooling and heating as a sequence of temperature jumps ΔT (not constant in general). The final result for TNM is

$$T_f(t) = T_0 + \int_{T_0}^{T} \left(1 - \exp\left\{-\left[\int_0^t \frac{dt'}{A_{TNM} \exp\left\{\frac{xh}{RT'(t')} + \frac{(1-x)h}{RT_f(t')}\right\}}\right]^{\beta}\right\}\right) dT' \qquad (4.105)$$

and that for SH is

$$T_f(t) = T_0 + \int_{T_0}^{T} \left(1 - \exp\left\{-\left[\int_0^t \frac{dt'}{A_{SH} \exp\left\{\frac{B_{SH}}{T'(t')\left[1-T_2/T_f(t')\right]}\right\}}\right]^{\beta}\right\}\right) dT'. \qquad (4.106)$$

For eqs. (4.105) and (4.106) the integral within the square brackets is the reduced time integral eq. (4.70) and the occurrence of T_f on both sides of eqs. (4.105) and (4.106) illustrates nonlinearity. For computations the integrals are of course replaced by summations for which dT' is replaced by $\Delta T'$ and dt' is replaced by $\Delta t'$. For annealing $\Delta t'$ is variable and for large overshoots in C_p^N $\Delta T'$ is also variable, both of which are described in [83] and discussed below.

The agreement between computed TNM and experimental C_p^N is generally excellent [79] for inorganic materials and thermal histories without annealing. The SH formalism does not generally improve on these results. For organic polymers and for thermal histories that include isothermal annealing [85,86], however, the agreement is less satisfactory. The reasons for these discrepancies are discussed below but include the fact that TNM parameters for organic polymers typically encompass a wider range, in particular the lowest values of x and β for polymers are much smaller than those for most inorganics [8].

4.9.2 Data Analysis

The general computation conditions used by Hodge and Heslin [83] are listed below. Unfortunately they cannot be compared with those of most (not all) other reports because the latter generally provide insufficient detail. Computation times for single thermal histories are typically about 2 s on modest computers (64 bit Intel i5 and AMD A6 CPUs). Optimization times are typically 20 – 30 minutes.

(a) The current value of ΔT is 0.1 K except for C_p^N overshoots in excess of 1.0. For the latter the temperature steps are reduced in inverse proportion to C_p^N for the previous step – for example for $C_p^N = 2.5$ the following temperature step is $0.1/2.5 = 0.04$ K. Computed C_p^N at regular temperature intervals needed for comparison with experiment are obtained by cubic spline interpolation.

(b) The introduction of annealing into TNM calculations of DSC thermal histories was initiated by Hodge and Berens [85]. They studied only the effects of isothermal annealing during cooling and the following discussion is restricted to that thermal history. Annealing times are divided into 100 logarithmically even intervals per decade [83], from 0.1s to the annealing time t_a in seconds, using the Matlab®/GNU Octave *logspace* function. For example for t_a = 24 hours $= 8.64\times10^4$ s the number of annealing intervals is 594. Very long annealing times increase the calculation time significantly beyond the 2 s or so needed for Matlab®/GNU Octave codes for thermal histories without annealing.

(c) The WW function is used explicitly (rather than being approximated as a Prony series as done earlier to reduce computation times that are no longer problematic).

(d) The Matlab®/GNU Octave *fminsearch* (simplex) function is used for optimization. This algorithm allows optimization of all four TNM and SH parameters and does not readily get trapped in a local rather than a global minimum.

(e) Normalized heat capacities C_p^N and dT_f / dT are almost always equated even though this is known to be an approximation. In some cases the differences are significant [48] but this has yet to be studied in detail [76].

(f) Thermal lag effects are corrected for by using experimentally determined thermal constants τ_{th}. Their values can be determined τ_{th} by observing the changes in heat flow and actual heating rate as a function of time in response to a programmed change in heating rate [83].

The effects of τ_{th} have been extensively discussed ever since the DSC technique was introduced (see refs in [8]) and have been analyzed in detail by Hodge and Heslin [83] with regard to the TNM formalism. In [83] the two were similar in shape but displaced from one another by an approximately constant time interval, implying an exponential Heaviside response function with a time constant of about 17±2 s (see table of Laplace transforms in Appendix 1A of Chapter One). When the researchers corrected for a thermal time constant of 15 s the experimental C_p^N data $\left(\text{e.g. } C_{p,\max}^N = 1.5\right)$ were independent of the ratio Q_h/Q_c within uncertainties as predicted by the TNM model (including a Q_h/Q_c = 25 K/min history for which the original data exhibited no overshoot at all). Since the TNM model gives a very good account of C_p^N when $Q_c = Q_h$ the confirmation of this particular prediction using an exponential

Heaviside response function suggests that the latter is a good approximation. The expression for deconvoluting observed experimental data $C_{p,obs}^{N}$ to produce the true "original" $C_{p,orig}^{N}$ is

$$C_{p,orig}\left(t\right)=C_{p,obs}\left(t\right)+\tau_{th}\left(\frac{dC_{p,obs}\left(t\right)}{dt}\right) \tag{4.107}$$

or

$$C_{p,orig}\left(T\right)=C_{p,obs}\left(T\right)+\tau_{th}Q_{h}\left[\frac{dC_{p,obs}\left(T\right)}{dT}\right]. \tag{4.108}$$

As noted in [83] eqs. (4.107) and (4.108) correct a typo in [8] in which $C_{p,orig}$ and $C_{p,obs}\left(t\right)$ were essentially interchanged. A similar analysis is implied in publications by Hutchinson et al. [87,88] although no details were given.

4.9.3 Sub-T_g Annealing Endotherms

As noted above Hodge and Berens [85] were the first to apply the TNM formalism to thermal histories that included annealing. When they applied it to the polymer PVC they found that it required TNM parameters x and β far smaller than any of those reported for inorganic materials. These extreme parameters produced a surprising result – upon reheating the enthalpy lost during annealing is sometimes recovered well below the glass transition temperature range to produce a sub-T_g peak in the heat capacity (so called Hodge peaks). These peaks are well reproduced by the TNM and SH formalisms. Similar annealing peaks have also been observed for PMMA [86] (albeit closer to T_g) and have also been well reproduced by the TNM and SN formalisms [86].

The probable explanation of these peaks was not recognized in 1995 when the effects of annealing on polymers were reviewed [41] and were therefore not mentioned. To explain the peaks it is first useful to be reminded that nonexponential decay functions such as WW can be expressed as a Prony series [§1.4.3.1] of exponential decay functions with different relaxation times and weighting factors that are the equivalent of a distribution of relaxation times:

$$\phi\left(t\right)=\sum_{n=1}^{N}g_{n}\exp\left(\frac{-t}{\tau_{n}}\right)_{i}. \tag{4.109}$$

Lesikar and Moynihan [89,90] introduced a formal order parameter description of the glass transition that associates each τ_n with a fictive temperature $T_{f,n}$ such that

$$T_{f}=\sum_{n=1}^{N}g_{n}T_{f,n} \tag{4.110}$$

with

$$\sum_{n=1}^{N}g_{n}=1. \tag{4.111}$$

When each τ_n was initially made a function of $T_{f,n}$, they found that the fits to experimental data were worse than τ_0 (and hence all τ_n) being determined by the global T_f. This is the key to why sub-T_g endotherms can occur. During initial heating of an annealed glass with low T_f and long τ_0 the shortest τ_n components relax first and contribute to a decrease in $\langle\tau\rangle \approx \tau_0$ so that the global T_f increases towards the un-annealed value and $C_p^N \approx dT_f / dT$ also increases. Equivalently the initially rapid decrease in $\phi(t)$ for a nonexponential decay function such as WW also enables partial relaxation to occur and therefore changes the global τ_0 and T_f. The decrease in the global τ_0 makes further changes in C_p^N more rapid well below T_g (that is determined by the longer components of τ_0). As T_f approaches the glassy T_f' that existed before annealing its rate of approach towards T_f' then decreases and C_p^N decreases until the onset of the glass transition temperature range is approached at T_f' - this produces the observed sub-T_g Hodge peak in C_p^N. This analysis also explains why sub-T_g endotherms that occur well below the T_g range are essentially superimposed on the glass transition for unannealed glasses.

4.9.4 TNM Parameters

There are rough correlations between the TNM parameters $1/x$ and h and between x and β [32,33,86] but they are weak and are at best suggestive of rather than compelling evidence for some possible underlying cause. The WW β parameter has the least uncertainty and the value of h can be obtained without TNM optimization so that in principle any correlation between h and β will have the smallest statistical uncertainty, but remarkably no plot of h versus β has ever been published to this author's knowledge. For most of the data exhibited in Table 1 in [8] (the omitted data are those for which β is not listed) such a plot indeed reveals less scatter but the correlation remains weak, as indicated by the correlation coefficient 0.64 for h versus β compared with 0.42 for h versus x and 0.41 for x versus β.

4.9.5 SH Parameters

Equations (4.88) and (4.89) have been confirmed for those cases when the SH model is directly fitted. Most experimental SH parameters are however obtained from TNM fits using these equations because TNM parameters are much more common (many pre-date the introduction of the SH formalism). As noted above the latter does not generally give improved fits compared with TNM [26] but nonetheless the SH parameters can be more plausibly linked to possible molecular factors such as rotational energy barriers $\Delta\mu$.

The starting point for discussing the AG parameters s_c^* and $\Delta\mu$ is eq. (4.64). This equation indicates that the heat capacity term C and s_c^* are needed before $\Delta\mu$ can be obtained from experimental values of B_{SH}. For this purpose it is convenient to define $\Delta C_p(T)$ as

$$\Delta C_p(T) = C' T_g / T \qquad (4.112)$$

so that C' equals $\Delta C_p\left(T_g\right)$ and eq. (4.64) becomes

$$B_{SH} = \frac{N_A s_c^* \Delta\mu}{k_B C' T_g} = \frac{N_A s_c^* \Delta\mu}{k_B T_g \Delta C_p\left(T_g\right)} = \frac{N_A \ln\left(\Omega\right)\Delta\mu}{T_g \Delta C_p\left(T_g\right)} \quad (4.113)$$

The unit of mass also needs to be defined and for this the concept of a "bead" introduced by Wunderlich [91] is helpful. Generally speaking the bead is the monomer segment of a polymer (such as $–CH_2–$ in polyethylene) and for small molecules it is a similarly small chemical entity (for example toluene is regarded as having two beads corresponding to the phenyl ring and the methyl substituent). For inorganics the bead is considered to be a rotatable unit such as a sulfate or nitrate, either as ions or groups covalently bound to a larger molecule. These examples indicate that the bead is an intuitive rather than a rigorous metric for mass. Wunderlich observed that $\Delta C_p\left(T_g\right)$ per bead was approximately constant for all materials that he studied (mostly polymers).

The value of s_c^* is also intuitive and is therefore fraught with uncertainties – see eq. (4.10) and the comment after it. The most commonly assumed value is

$$s_c^* = k_B \ln 2 \quad (4.114)$$

because there is a minimum of two configurations – those before and after rearrangement. At least two exceptions to this have been discussed however. First, Sales [92] reversed the logic by equating $\Delta\mu$ with the P – O bond strength and discussed the consequent values of s_c^* in terms of the coordination number of phosphate around various cations. He found that the differences in s_c^* values were consistent with the known differences in coordination geometries of the cations. Second, Hodge [26] suggested that eq. (4.114) is inappropriate for polymers because of constraints imposed by consecutive covalent bonds, and eq. (4.114) was replaced by $s_c^* = k_B \ln 3! = k_B \ln 6$ (arbitrary) and then by [93]

$$s_c^* = k_B \ln 2^3 = k_B \ln 8 \quad (4.115)$$

because "…two rotational states are available to each segment and [a] crankshaft motion is assumed to involve 3 segments…". If three distinguishable rotational states per segment and two subsequent segments are assumed (no crankshaft motion) then

$$s_c^* = k_B \ln 3^2 = k_B \ln 9\,. \quad (4.116)$$

The difference between ln 8 and ln 9 is smaller than any reasonable uncertainty in s_c^*. For large nonpolymeric molecules that are linear the crankshaft motion is probably irrelevant and it is reasonable to extend eq. (4.116) to

$$s_c^* = k_B \ln 3^{N-1} \quad (4.117)$$

where N is the number of beads (segments) and N-1 is the number of rotatable bonds between them. Equation (4.117) has not been suggested before and like eq. (4.115) for polymers it has dubious statistical rigor so that values of $\Delta\mu$ derived from it must still be regarded as approximate. Because of internal (and presumably external) geometrical constraints the number of configurations for large molecules is almost certainly less that that given by eq. (4.117) and values of $\Delta\mu$ should therefore be regarded as minimum ones. An interesting numerical convenience is that $s_c^*/k_B \approx N \pm 1$ because eq. (4.117) is equivalent to $s_c^* = k_B\left(N-1\right)\ln 3$, $\ln 3 \approx 1.1$ and $\left(N-1\right) \approx 0.9N$ for values of N around 10 that are often encountered.

Hodge and O'Reilly [93] analyzed the SH parameters for five non-polymeric organic molecules: the ortho-, meta- and para- (o-, m-, p-) isomers of indane, o-terphenyl (OTP), and tri-α-naphthyl benzene (TNB). The chemical formulae for these materials are given in [93]. Their data are discussed in detail here (more than given in the original publication) for three reasons: (i) re-evaluations of s_c^* using eq. (4.117); (ii) revised SH values of $\Delta\mu$ based on these new values of s_c^*; (iii) confusion about units. Data from [93] are summarized in Table 4.1 that combines entries in Tables 1 and 4 of [93] as well as results from the new calculations. SH parameters are rounded off to two significant figures. The values of N correspond to the original number 11 as well as the number of Wunderlich segments for the three indane isomers cited in [93]. The units of $\Delta\mu$ are kJ mol^{-1}, not kJ (mol-bonds)$^{-1}$ as stated in [93]. The boldface $\Delta\mu$ entries in Table 4.1 correspond to the values of N associated with each material – the other entries are given for comparison.

TABLE 4.1

QUANTITY	o-indane	m-indane	p-indane	OTP	TNB
T_g (K)	357	359	385	240	340
$\Delta C_p(T_g)$ [JK^{-1}mol^{-1}]	161	198	182	113	150
B (K)	4500	2600	7400	4400	2100
T_2 (K)	280	300	280	180	260
$\Delta\mu$ (N=10) [kJmol^{-1}]	95	63	190	**68**	42
$\Delta\mu$ (N=11) [kJmol^{-1}]	**86**	**56**	**170**	61	38
$\Delta\mu$ (N=13) [kJmol^{-1}]	71	47	140	51	**31**
$\Delta\mu$ (N=14) [kJmol^{-1}]	**66**	43	130	47	29
$\Delta\mu$ (N=16) [kJmol^{-1}]	57	38	**110**	41	25
$\Delta\mu$ (N=17) [kJmol^{-1}]	53	**35**	110	38	23

The values of $\Delta\mu$ need to be divided by N-1 to obtain estimates of average inter-segmental rotational energy barriers ΔE. Using N = 11 for the (o-, m-, p-) indanes yields ΔE = 9, 6, 17 kJ/bond that are smaller than typical rotational energy barriers for isolated molecules by a factor of 2 or so and probably by more for molecules constrained in condensed media, but as noted above the cited $\Delta\mu$ values should be regarded as minimum ones. The Wunderlich N values for the o-, m- and p- indane isomers are 14, 17 and 16 respectively and these give even smaller values of ΔE. For OTP the number of Wunderlich segments is 113/11.3 = 10 and the average rotational energy barrier is 61kJ/10 = 6.1 kJ, and for TNB the number of Wunderlich segments is 150/11.3 = 13 and the average rotational energy barrier is 38kJ/12 = 3 kJ. Both these barrier energies are also too small but are again minimum ones.

The weak correlations between the TNM parameters become stronger when they are expressed in terms of SH parameters. In particular when the SH parameter $T_g / T_2 \approx (1-x)^{-1}$ is plotted against $B_{SH} \approx x^2 h / R$ and materials are separated into plausible molecular types [32,33] three linear correlations are clearly evident (if two suspiciously outlying polystyrene data are removed the polymer correlation is even better). There is an indisputable extrapolation towards $T_g/T_2 \to 1$ as $B_{SH} \to 0$ for each of the three correlation lines. Since B_{SH} is proportional to $\Delta\mu$ in the AG model and the proportionality constant cannot be zero the extrapolation $B \to 0$ corresponds unambiguously to $\Delta\mu \to 0$ and strongly suggests that as $\Delta\mu$ approaches zero there is no (average) barrier to prevent T_g approaching some fundamental amorphous state temperature that is approximated by T_2 and/or T_K ("ideal glass", see §4.2.2.6). This in turn suggests yet again that some fundamental lower limit to T_g is possible that could have thermodynamic roots and could even be a candidate for Fermi's "not theoretically impossible" state of small but nonzero entropy at 0 K (§4.2.2.6 and [1]).

APPENDIX A:TOC and corrections to ref [8]

There are several errata and one omission in this paper that are corrected here. Published errata are incomplete and the omission is the table of contents given here:

TABLE OF CONTENTS

Errata

A published errata was not complete. The following list is complete:

(1) Page 222: The first term of eq. (44) should be $T^{-1}\Delta C_p dT$.

(2) Equations (57) – (60) [page 225] are incorrect. The time derivatives on the right should be of C_p, not C_p^* as written.

(3) The following should be deleted: end of the first paragraph in column 2 of page 225 starting from "Applying Eqs. (57) - (60) to…" to " computed temperature dependence of $C_P^*(T)$".

(4) Page 228: Equation (80) and the preceding line should be deleted.

(5) Page 228: The line shortly following eq. (81) beginning "Eq. (80) has not been…" to "mathematical libraries." should be deleted.

(6) Page 239: Three lines after eq. (167): Eq. (158) should be Eq. (163).

(7) Half way down the first paragraph of 4.7.1 the equation for T_f should be $T_f = T\text{-}KP$.

(8) Reference [16] should be to J. H. Gibbs, not H. J. Gibbs.

(9) Reference [240]: the page number should be 663, not 633.

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