CHAPTER FOUR (15)
STRUCTURAL RELAXATION
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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 (not crystalline) equilibrium state 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 the glass transition. There are two principle differences between the kinetics of structural relaxation and the other relaxations considered in earlier chapters. The first 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". The second difference is that 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".

The SI unit for temperature (Kelvin, symbol K) is used throughout. As usual constant pressure processes are referred to as isobaric, those at constant volume as isochoric, and those at constant temperature as isothermal. 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), Rankin (^{o}R), and 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 Fahrenheit temperatures in the low teens), 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 the melting temperature of ice 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 ^{o}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 Rankin scale is based on an absolute zero that occurs at about –459.7^{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. When using the mol it is important to be aware of the question "mol of what?". 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 point particles (see any introductory physics or physical chemistry text). A noteworthy result of the 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 $\left(V-nb\right)$ 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 $\left(n/V\right)$, 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 $\left(n/V\right)$ of particles. Thus the pressure is reduced in proportion to $\left(n^2/V^2\right)$ and the Van der Waals equation becomes

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

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*

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

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 the exact 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

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

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. Equation (4.7) adheres to the convention that *W* is positive for work done *on* the system. An alternative 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 and actually increases for irreversible processes. 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]). More probable states thus 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

$$C_p = \left(\frac{\partial Q}{\partial T}\right)\bigg|_P$$

and (4.11)

$$C_v = \left(\frac{\partial Q}{\partial T}\right)\bigg|_V ,$$

where δQ has been replaced by ∂Q 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 capacity has the same units as entropy but the two are physically 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 $C_p \geq C_v$ [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 Debye heat capacity 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 thus 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 oscillators is [6]

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

where Θ_D is the Debye temperature corresponding to a maximum cutoff energy for the distribution of phonon energies and $x_D=\theta_D/T$. 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 of the best expressions of which is probably that due to 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.

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

$$H = U + PV;$$

$$dH = \left(TdS - PdV\right) + \left(VdP + PdV\right) \qquad (4.18)$$

$$= TdS + VdP.$$

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:

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

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

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 bases but entropically expensive because it is more ordered compared with the disorder of separated strands and more disordered ambient water molecules. The coding and decoding of DNA therefore depends on the small difference between large enthalpy and entropy factors.

4.3.5 Chemical Potential μ

For a species *i* this quantity is denoted by μ_i and is needed when there are a number of different entities in a system. If this number is n_i for species *i* then [3]

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

Which derivative is chosen depends on the variables in which μ_i is to be 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

$$\mu_i^E = \mu_i + z_i e\varphi \qquad (4.22)$$

(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

$$d\mu = -sdT + vdP, \qquad (4.23)$$

where *s* and *v* are the entropy and volume per entity (cf. eq. (4.20)). Equation (4.23) does not apply to an individual entity however – 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

$$dU = -PdV + TdS \Rightarrow \left.\frac{\partial U}{\partial V}\right|_T = -P + T\left(\frac{\partial S}{\partial V}\right)_T . \qquad (4.24)$$

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

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T , \qquad (4.25)$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T , \qquad (4.26)$$

and

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P \qquad (4.27)$$

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

$$C_P - C_V = \left.\left(\frac{\partial H}{\partial T}\right)\right|_P - C_V = \left.\left(\frac{\partial U}{\partial T}\right)\right|_P + \left.\left(\frac{\partial(PV)}{\partial T}\right)\right|_P - C_V . \qquad (4.28)$$

4.4 Maxwell Relations

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

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V , \qquad (4.29)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \Leftrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V , \qquad (4.30)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P . \qquad (4.31)$$

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

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right), \qquad (4.32)$$

obtained from

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_T \Rightarrow \left(\frac{\partial C_p}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial P \partial T}\right) \qquad (4.33)$$

so that

$$\left.\left(\frac{\partial S}{\partial P}\right)\right|_T = -\left.\left(\frac{\partial V}{\partial T}\right)\right|_P \Rightarrow \left(\frac{\partial^2 S}{\partial P \partial T}\right) = -\left.\left(\frac{\partial^2 V}{\partial T^2}\right)\right|_P . \qquad (4.34)$$

Another example is [2]

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P . \qquad (4.35)$$

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. 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 are sometimes related to thermodynamic functions. For example [3]

$$k_B C_p = \langle \Delta S^2 \rangle \qquad (4.36)$$

and

$$k_B T V \kappa = \langle \Delta V^2 \rangle . \qquad (4.37)$$

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

$$\phi(T) = \overline{x(t)x(t+T)} \qquad (4.38)$$

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

4.6 Egodicity and the Deborah Number

Egodicity is a statement about the equivalence of probabilities in terms of time averages and various ensemble averages in statistical mechanics. The ensembles are distinguished by 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. A "very long time" can be 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. 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 incorrect. 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 distilled. Two definitions by Boltzmann are discussed. 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 introduced the same 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 ε_i under the constraints that the total energy $E=\sum n_i\varepsilon_i$ 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 [5], "more like a declaration". Ergodicity asserts that Boltzmann's two definitions are equivalent and as Pais also 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 is 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. Relaxation times of years or even millennia are confidently estimated below T_g so observation times are necessarily much smaller. The DN is also usefully defined as [8]

$$DN \equiv \frac{d\tau}{dt} = \left(\frac{d\tau}{dT}\right)\left(\frac{dT}{dt}\right) = \left(\frac{d\tau}{dT}\right)Q_c\,, \qquad (4.39)$$

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 (but could perhaps be approximated as Ehrenfest third order transitions). In any event 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 range 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. However the various first derivatives of ΔV, ΔH and ΔS are not zero 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

$$d\Delta V = 0 = \left(\frac{\partial \Delta V}{\partial T}\right)_P dT + \left(\frac{\partial \Delta V}{\partial P}\right)_T dP = V\left(\Delta\alpha dT - \Delta\kappa_T dP\right) \tag{4.40}$$

from which

$$\left(\frac{\partial T_2}{\partial P}\right)_V = \frac{\Delta\kappa_T}{\Delta\alpha}, \tag{4.41}$$

where eqs. (4.13) and (4.14) for $\Delta\alpha$ and $\Delta\kappa_T$ have been used. Deviations from eq. (4.41) have often been reported for $T_g=T_2$ (see §4.8.3.3), 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. (4.41).

For enthalpy

$$d\Delta H = \left(\frac{\partial \Delta H}{\partial T}\right)_P dT + \left(\frac{\partial \Delta H}{\partial P}\right)_T dP = \Delta C_p dT + \left[\Delta V - T\left(\frac{\partial \Delta V}{\partial T}\right)_P\right] dP = 0 \tag{4.42}$$

but since $\Delta V = 0$ then

$$\left(\frac{\partial T_2}{\partial P}\right)_H = VT\frac{\Delta\alpha}{\Delta C_p}. \tag{4.43}$$

For entropy

$$d\left(\Delta S\right)=0=\left(\frac{\partial\Delta S}{\partial T}\right)_P dT+\left(\frac{\partial\Delta S}{\partial P}\right)_T dP=\left(\frac{\partial\Delta S}{\partial T}\right)_P dT-\left(\frac{\partial\Delta V}{\partial T}\right)_T dP$$
$$=T^{-1}\Delta C_p dT-V\Delta\alpha dP \quad (4.44)$$

so that

$$\left(\frac{\partial T}{\partial P}\right)_{\Delta S}=VT\frac{\Delta\alpha}{\Delta C_p}. \quad (4.45)$$

Note that eqs. (4.43) and (4.45) are the same.

In anticipation of the nonlinear Adam-Gibbs model for structural relaxation discussed in §4.8.3 an expression for $\partial T_2/\partial P$ based on TS_c being constant is now given. The condition that TS_c be constant implies

$$\begin{aligned} d\left(TS_c\right)&=TdS_c+S_c dT=0\\ &=\Delta C_p dT-TV\Delta\alpha dP+S_c dT\\ &=\left(\Delta C_p+S_c\right)dT-TV\Delta\alpha dP \end{aligned} \quad (4.46)$$

so that

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

The Prigogine-Defay ratio Π is defined by

$$\Pi\equiv\frac{\left(\partial T_2/\partial P\right)\big|_{\Delta V}}{\left(\partial T_2/\partial P\right)\big|_{\Delta S}}=\frac{\Delta C_p\Delta\kappa_T}{TV\left(\Delta\alpha\right)^2}. \quad (4.48)$$

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 $\Pi>1$ for $T_2=T_g$ 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 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. This section is divided into three segments 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 (as well as many liquids above the melting temperature) rarely conform to the Arrhenius temperature dependence

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

where E_a is the Arrhenius activation energy and A_A is a constant. Instead they 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):

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

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

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

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

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

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^*. 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

$$B_F=2.303C_1C_2, \tag{4.54}$$

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.

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 small mathematical issues related to fragility but these criticisms do not detract from the immense overall value of the concept.

There are two complementary definitions of fragility, thermodynamic and kinetic, that reflect the intricate and debated relation between the thermodynamic and kinetic aspects of the glass transition phenomenon (such a 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 produce 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 $\tau_0\left(T\right)$, the latter being generally well described by the Fulcher equation. The kinetic 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 $T \approx T_g\left(T_g/T \approx 1\right)$ and $\tau_0 = 10^{-14}$ s (vibrational lifetime) as $T \to \infty\left(T_g/T \to 0\right)$. 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 (A_F in eq. (4.50) for example) that is often just termed *A* in the literature and can be confused with A_A. 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. Angell [19] has described how $m_{\min}$ predicts the "universal" WLF parameter $C_1 \approx 17$.

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 $\Delta C_p\left(T\right) = C/T$ 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 [20], Goldstein [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 need to rearrange cooperatively for relaxation to occur. The transition state activation energy E_A is approximated 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

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

where $S_c(T)$ is the macroscopic configurational entropy (defined in eq. (4.61) 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). Explicitly

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

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

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 $S_c(T)$ is zero, denoted as such to emphasize that its equivalence with the thermodynamic Kauzmann temperature T_K (discussed below) needs to be established experimentally. Assessment of $\Delta C_p(T)$ is not trivial. It must be obtained by extrapolations of $C_p(T)$ 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 function $\Delta C_p(T)$ also depends on how C_{pl} is extrapolated. 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 adopted here is that all the contributions to $\Delta C_p\left(T_g\right)$ of whatever type contribute to 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

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

so that

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

i.e. the Fulcher form is recovered 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 [31]. However since eqs (4.63) and (4.67) are almost indistinguishable the AG model can probably accommodate most approximations to the Fulcher equation that are found experimentally [32,33].

Equations (4.59) 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 $T \to T_2$ and simplistically this divergence can be expected to prevent T_g approaching T_2 [26,34] (assuming that T_2 is indeed some sort of ideal T_g). 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 §4.8.3).

The assertion made above that the kinetic and thermodynamic definitions of fragility are 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 nonequilibrium state they can isothermally relax towards the equilibrium state. A discussion of this phenomenon has been given by Hodge [8,39]. There are two canonical 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 cannot be ignored for even small perturbations, and it 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). The 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 good 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 has the dimensions of $t^{1-\mu}$ and is dependent on material and annealing temperature. The quantity $\mu \le 1$ is an empirical parameter referred to here as the Struik shift parameter. The nonlinearity of relaxation expressions that contain 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 $\tau(t') = \tau_0^{1-\mu} t'^{\mu}_a$

$$\xi(t)=\frac{(t/\tau_0)^{(1-\mu)}}{(1-\mu)} \qquad \left[\xi(-\infty)=0\right]. \tag{4.71}$$

For the WW function [8]

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

where

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

and

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

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].

Quantification of nonlinearity is simplified by defining a metric for the nonequilibrium state. The fictive temperature T_f introduced by Tool [45-47] is such a metric. It was originally suggested in an oral presentation in 1924, so that 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. Since T_f can be associated with any property the phenomenologies described below can be applied to any property. For enthalpy H, whose relaxation phenomenology is representative of all properties, T_f is defined by

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

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)

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

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)].

For polymers mechanical stresses (shear and tensile), hydrostatic pressure, and swelling induced by vapor absorption followed by rapid desorption, all decrease the average isothermal structural relaxation time in the glasses. 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] often approximate applied stresses and pressure as 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 a shorter structural relaxation time. The fact that relaxation is faster at a smaller volume is inconsistent with the free volume models frequently used by polymer physicists [52] but is consistent with enthalpy/entropy models such as Adam-Gibbs.

4.8.3 The Glass Transition

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 mainly considers the relaxation aspects of the glass transition phenomenon, although a brief general overview of it is 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. When asked at the end of the 20th century about the most important challenges awaiting 21st century science, Nobel laureate Philip Anderson stated in *Science* [56] that "The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. …". He had earlier 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.

Glass Transition Temperature

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. There is also confusion about the glass "transition" because it is not a transition in the traditional sense but rather a phenomenon that occurs over an unexpected and thus far theoretically unexplained narrow temperature range. 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. An excellent account of the physics of the glass transition as a condensed matter phenomenon is given in Angell's review article [7].

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 by other nonthermal processes, only the heating rate is known but should still be specified. The three definitions are:

(a) *Midpoint*. The center of the transition temperature range.

(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 $C_{pg}(T)$ 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 typically has a similar value to the onset definition if the heating and cooling rates are comparable.

As noted the first two definitions apply to both cooling and heating but values from cooling data are preferred. One 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 this issue consider the question "what is 'T_g' for an annealed glass compared with a non-annealed glass?" The answer depends on how T_g is defined. As just noted the best definition of T_g is the glassy state value of the fictive temperature T_f' and this *decreases* with annealing. However upon reheating enthalpy recovery occurs at higher temperatures because of nonlinearity – the lower glassy fictive temperature lengthens 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 and onset definitions of T_g *increase*.

The value of "T_g" that has been discussed above is generally 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 value of T_g simply shifts the transition range along the temperature axis. One exception to this is that annealing behavior at temperature T_a is a strong function of $T_g – T_a$. Another exception is the composition dependence of "T_g" for binary mixtures of materials with very different values of T_g (polymer/solvent mixtures for example), that illustrates the flexibility of WW-type functions. The dependence of T_g on the concentration c of the lower T_g component is often well described by

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

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 the 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).

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 at a temperature well above absolute zero. At this temperature the entropy of the supercooled liquid equals 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 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 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 some polymers the uncertainty is even larger because of a 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. However, as noted in the discussion of the Adam-Gibbs model (§4.8.1), it is possible that all contributions to $\Delta C_p(T)$ contribute to the relaxation kinetics so that how ΔC_p is partitioned is irrelevant. In any event 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 are 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 nonzero T_K seems almost certain in these cases. There is also the possibility that the heat capacity decreases rapidly to nearly zero rather than mathematical zero at a temperature where the entropy is also small but nonzero. These ideas are quantified in the next paragraph about a possible Ehrenfest 2nd order transition resolving the Kauzmann problem.

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]). Also, a thermodynamic mechanism for crystallization always preventing low values of entropy to be attained has apparently not yet been suggested.

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 some 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

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

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 many polymers [31]. Preliminary results [76] indicate that a good fit 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 about three times smaller than $T_{\max}$ [76]. Other preliminary calculations [76] suggest that good Fulcher fits also obtain 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

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

for $T < T_{\max}$. Larger values of f produce sharper low frequency decreases in $C_p(T)$ that in the limit $f \to \infty$ approaches the instantaneous decrease approximation. These heat capacity functions also yield good Fulcher fits with T_0 values that approach the temperature $T_{1/2} < T_{\max}$ at which ΔC_p is half the maximum. Preliminary analyses [76] suggest that the ratio $R = T_0/T_{1/2}$ is approximately given by

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

Angell [77] has 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 ansatz for relaxation times because it only affects the calculation of T_K and does not affect S_c apart from its behavior zero deep in the glassy state, and the latter does not affect the Adam-Gibbs model above T_g.

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 below T_g, the values of T_g are almost independent of composition [78]. A composition invariant T_g has also been observed in the LiCl-H_2O system in which phase separation is directly observed [69,79]. 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.

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 only 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 [80] is a generalization of the Arrhenius equation:

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

where $0<x\le 1$ is often referred to as the nonlinearity parameter. The value of h can be obtained from [80]

$$\frac{h}{R}\approx\frac{-d\ln\dot{T}_c}{d\left(1/T_f{}'\right)} \tag{4.83}$$

but the uncertainties are large (typically about ±20%).

The NLAG ("Nonlinear Adam-Gibbs") or SH ("Scherer-Hodge") expression [25,26] is obtained from the AG equation (4.60) by assuming that S_c is a function of T_f rather than of T:

$$S_C\left(T_f\right)=C\left(1-T_2/T_f\right) \tag{4.84}$$

so that

$$\tau_0\left(T,T_f\right)=A_{SH}\exp\left[\frac{B_{SH}}{T\left(1-T_2/T_f\right)}\right]. \tag{4.85}$$

Equation (4.85) has been called by several other names: Adam-Gibbs-Vogel (AGV), Adam-Gibbs-Fulcher (AGF), in addition to NLAG and Scherer-Hodge (the last name is not this author's choice but is increasingly common and so is used henceforth). The full and partial temperature derivatives of eq. (4.85) are

$$\frac{d\ln\tau_0(T)}{d(1/T)}=\frac{B_{SH}}{(1-T_2/T)^2}=\frac{h}{R} \tag{4.86}$$

and

$$\left[\frac{\partial\ln\tau_0(T)}{\partial(1/T)}\right]_{T_f}=\frac{B_{SH}}{\left(1-T_2/T_f\right)}=\frac{xh}{R}. \tag{4.87}$$

Applying eqs. (4.86) and (4.87) 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]

$$x \approx 1-T_2/T_g; \tag{4.88}$$

$$T_2 = T_g(1-x) \tag{4.89}$$

and

$$B_{SH} \approx x^2 h/R \approx \left(1-T_2/T_g\right)^2 h/R; \tag{4.90}$$

$$\frac{h}{R}=\frac{B_{SH}}{\left(1-T_2/T_g\right)^2}, \tag{4.91}$$

where T_g refers to the onset definition that is closer to the glassy state. Equation (4.91) is a generalization of eq. (4.51) that applies to the nonequilibrium glass transition temperature range. Equations (4.88) - (4.91) 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_{cg} [8] is

$$x_{AG} \approx \frac{S_{cg}}{S_{cg}+\Delta C_p\left(T_g\right)}, \tag{4.92}$$

where again T_g refers to the onset definition. Equation (4.92) predicts lower values of x for larger values of $\Delta C_p(T_g)$ and smaller values of S_{cg}.

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 [81] in which it was noted that μ depends on the annealing temperature T_a and the WW nonexponentiality parameter β as well as the nonlinearity parameter 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 general inverse relation between x and m seems probable although a rigorous mathematical derivation is not yet at hand. However a more general analysis than SH is now 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. The relation

$$\tau_0\left(T,T_f\right)=A_{mx}\exp\left[f(T)g\left(T_f\right)\right] \tag{4.93}$$

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

$$m=\left[\frac{1}{RT_g\ln(10)}\right]\left\{f(T)\left[dg(T)/d(1/T)\right]+g(T)\left[df(T)/d(1/T)\right]\right\}. \tag{4.94}$$

Full and partial differentiation of eq. (4.94) with respect to 1/*T* yields

$$\frac{h}{R}=\frac{d\ln\tau_0\left(T_f=T,T\right)}{d(1/T)}=g(T)\frac{df}{d(1/T)}+f(T)\frac{dg}{d(1/T)}\bigg|_{T=T_g} \tag{4.95}$$

and

$$\frac{xh}{R}=\frac{\partial\ln\tau_0\left(T_f,T\right)}{\partial(1/T)}\bigg|_{T=T_f=T_g}=g\left(T_g\right)\frac{df}{d(1/T)}\bigg|_{T=T_g}, \tag{4.96}$$

so that

$$\frac{1}{x}=\frac{g\dfrac{df}{d(1/T)}+f\dfrac{dg}{d(1/T)}}{g\dfrac{df}{d(1/T)}}\Bigg|_{T=T_f=T_g}=\left[1+\frac{d\ln g/d(1/T)}{d\ln f/d(1/T)}\right]\Bigg|_{T=T_f+T_g}. \tag{4.97}$$

Equations (4.94) and (4.97) yield

$$x^{-1}=\frac{mRT_g\ln(10)}{gdf/d(1/T)}\bigg|_{T=T_f=T_g}. \tag{4.98}$$

The function $df/d(1/T)\big|_{T_g}$ must be approximately equal to *xh*/*R* to ensure consistency with the experimentally observed TNM equation so that

$$\frac{mR^2T_g\ln(10)}{hg\left(T_g\right)}\approx 1. \tag{4.99}$$

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 exactly inversely proportional to *x*.

Thermorheological Complexity

All the analyses discussed so far consider the TNM and SH parameters to be independent of temperature. However there are several reports scattered throughout the literature that some of these parameters are temperature dependent, in particular that the distributions of relaxation times depend on both *T* and T_f. The following discussion of this possibility draws heavily from [82].

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

$$\ln\tau_i=\ln A_A+\frac{E_i}{RT}. \tag{4.100}$$

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 therefore

$$\sigma_{\ln\tau} = \frac{\sigma_E}{RT}. \tag{4.101}$$

Thus any distribution of relaxation times is temperature dependent if there is an underlying distribution of activation energies. Since any physically reasonable distribution of activation energies for condensed media is unlikely to be a delta function thermorheological simplicity must be regarded as an approximation. 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 yields, for a Gaussian distribution in B,

$$\sigma_{\ln\tau} = \frac{\sigma_B}{T\left(1 - T_2 / T_f\right)}. \tag{4.102}$$

Gaussian standard deviations have their counterparts in the widths of other distributions such as WW so that eqs. (4.101) and (4.102) are 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 [82]. For the WW decay function for example

$$\exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right] = \sum_{i=1}^{N} g_i\left(T, T_f\right) \exp\left[-\left(\frac{t}{\tau_i}\right)\right], \tag{4.103}$$

where the best fit values of both N and g_i depend on β. This is computationally expensive because the coefficients g_i must be recalculated at every temperature step although doing so every $n > 1$ steps may be a good approximation. Estimates by the present author suggest that computation times are probably around $10^{0\pm1}$ days, depending on $\beta\left(T_g\right)$.

4.9 Experimental DSC Results

The DSC technique ("Differential Scanning Calorimetry") 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. It is described 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.

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 be 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 could obviously condense). The heat capacity is then computed from

$$C_p(T) = \left(\frac{dq}{dt}\right) \Big/ \left(\frac{dT}{dt}\right) = \left(\frac{dq}{dt}\right) \Big/ \dot{T}_{c,h}, \tag{4.104}$$

where $\dot{T}_{c,h}$ is the cooling/heating rate and dq/dt is the measured differential heat input (typically given in mW). Note that for any given C_p the differential heat input dq/dt is proportional to $\dot{T}_{c,h}$

so that there is a lower limit to $\dot{T}_{c,h}$ that is determined by instrumental sensitivity.

Thermal lag shifts the DSC temperature calibration by an amount $\tau_{th}\dot{T}_h$ ([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 larger thermal conductivity of metals. 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 the 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 just implicit in the identification of the manufacturer and/or product name. Crystallinity and crystal morphology can also 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 reproducibility of the heat capacity 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. 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. (4.85), the reduced time eq. (4.70), and Boltzmann superposition (Chapter One). These calculations are discussed here because they illustrate many aspects of structural relaxation kinetics and provide many insights into the glass transition phenomenon.

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. (4.85) using time dependent T and T_f:

$$\tau_0(t) = A_{TNM}\exp\left[\frac{xh}{RT(t)} + \frac{(1-x)}{RT_f(t)}\right] \tag{4.105}$$

or

$$\tau_0(t) = A_{SH}\exp\left[\frac{B_{SH}}{T(t)\left[1-T_2/T_f(t)\right]}\right]. \tag{4.106}$$

This is the first step in computing $T_f[T(t)]$ and thence dT_f/dT. The second step is to introduce Boltzmann superposition by representing rate cooling and heating as a sequence of temperature jumps ΔT (typically constant but not necessarily so, see below). The final result for TNM is

$$T_f(t) = T_0 + \int_{T_0}^{T} \left(1 - \exp\left\{ -\left[\int_0^t \frac{dt'}{A_{TNM} \exp\left\{ \frac{xh}{RT'(t')} + \frac{(1-x)h}{RT_f(t')} \right\}} \right]^{\beta} \right\} \right) dT' \tag{4.107}$$

and that for SH is

$$T_f(t) = T_0 + \int_{T_0}^{T} \left(1 - \exp\left\{ -\left[\int_0^t \frac{dt'}{A_{SH} \exp\left\{ \frac{B_{SH}}{T'(t')\left[1 - T_2 / T_f(t')\right]} \right\}} \right]^{\beta} \right\} \right) dT'. \tag{4.108}$$

For eqs. (4.107) and (4.108) 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. (4.107) and (4.108) expresses nonlinearity. For computations the integrals are of course replaced by summations for which dT' is replaced by $\Delta T'$ and dt' is replaced by $\Delta t'$. The value of $\Delta t'$ is variable for annealing, and $\Delta T'$ is variable for large overshoots in C_p^N [83], as 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 and include the fact that the gamut of TNM parameters for organic polymers is typically larger, in particular the lowest values of x and β for polymers are much smaller than those of the lowest values for inorganic materials [8].

4.9.1 Data Analysis

The general computation conditions reported by Hodge and Heslin [83] are listed below. Unfortunately these conditions cannot be compared with those given in most other reports because the latter often provide insufficient detail. Computation times for thermal histories without annealing are typically about 2 s on modest computers using Matlab® or Gnu Octave, and optimization times for thermal histories that include annealing are typically 20 – 30 minutes.

(a) The currently used 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 values of dT_f/dT at the regular temperature intervals needed for comparison with experiment are obtained by cubic spline interpolation.

(b) Annealing times are divided into 100 logarithmically even intervals per decade, 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 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 minimum.

Thermal lag effects are corrected for by using experimentally determined thermal constants τ_{th}. The effects of τ_{th} have been 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. The Hodge/Heslin value of τ_{th} was determined from the changes in heat flow and measured heating rate as a function of time following a programmed change in heating rate and equating τ_{th} to the displacement of one from the other (15 s in this case). The curve shapes were approximately the same so that this displacement implied an exponential Heaviside response function with a time constant of 15 s. When the researchers corrected for this time constant of the experimental C_p^N data for no annealing were independent of the ratio $\dot{T}_h/\dot{T}_c$ within uncertainties, as predicted by the TNM model (including a $\dot{T}_h/\dot{T}_c$ = 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 $\dot{T}_h = \dot{T}_c$ the confirmation of this prediction using an exponential Heaviside response function indicates 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

$$C_{p,orig}(t) = C_{p,obs}(t) + \tau_{th}\left(\frac{dC_{p,obs}(t)}{dt}\right) \tag{4.109}$$

or

$$C_{p,orig}(T) = C_{p,obs}(T) + \tau_{th}\dot{T}_h\left[\frac{dC_{p,obs}(T)}{dT}\right]. \tag{4.110}$$

A similar analysis is implied in publications by Hutchinson et al. [87,88] although no details were given.

4.9.2 Sub-T_g Annealing Endotherms

As noted above Hodge and Berens [85] were the first to apply the TNM formalism to polymers and 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 was sometimes recovered well below the glass transition temperature range to produce sub-T_g peaks in the heat capacity. 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 are also well reproduced by the TNM and SN formalisms [86].

The explanation of these peaks was not recognized in 1995 when the effects of annealing on polymers were reviewed [41]. 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:

$$\exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right]=\sum_{n=1}^{N} g_n \exp\left(\frac{-t}{\tau_n}\right). \qquad (4.111)$$

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

$$T_f=\sum_{n=1}^{N} g_n T_{f,n} \qquad (4.112)$$

with

$$\sum_{n=1}^{N} g_n = 1. \qquad (4.113)$$

When each τ_n was initially made a function of $T_{f,n}$ they found that the fits to experimental data were worse than if τ_0 (and hence all τ_n) were 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 $\langle\tau\rangle$ 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. As T_f approaches the glassy T_f' that existed before annealing its rate of approach towards T_f' 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 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. Note that both nonexponentiality and nonlinearity come into play here. The more rapidly the initial decrease in T_f is during heating the faster the distribution moves to shorter times because of nonlinearity, and the rapidity of the initial decrease in T_f depends on nonexponentiality.

Not all sub-T_g endotherms are generated by enthalpy relaxation. There is always the possibility that they are produced by the melting of crystals or crystallites formed during annealing. An unpublished result by Hodge [91] provides a good example of how easily the two possibilities can be confused, especially if estimates of experimental uncertainties are too pessimistic. Hodge re-analyzed the DSC data of Johari et al. [92] on annealed hydrated proteins that exhibited broad and weak endotherms when scanned after annealing at several temperatures. The experimental uncertainties in the widths and peak heights of the endotherms were estimated to be large because of a sloping and curved background, but TNM parameters were nevertheless found that fitted the data much better than the initial set of parameters suggested in [92]: $\{\ln A(s)=-80; h/R=2.0\times10^4\ \text{K};\ x=1.0; \beta=0.04\}$. The largest discrepancy between observed and calculated endotherm properties was the annealing temperature dependence of the endotherm magnitudes but this was thought to be within experimental uncertainty. However, Tombari and Johari later reported [93] that the endotherms were almost certainly due to melting of crystals of NaCl.2H_2O in the commercial samples of the hydrated proteins, formed during annealing. Hodge's estimates of the experimental endotherm areas passed through a maximum at an annealing temperature 238K that was 14K below the melting temperature 252K of the crystals, near which a maximum rate of crystallization might reasonably be expected.

4.9.3 TNM Parameters

There are rough correlations between the TNM parameters 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, any 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 been published to this author's knowledge. For most of the data 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.

4.9.4 SH Parameters

Equations (4.89) and (4.90) have been confirmed for those cases when the TNM and SH models have been fitted to the same data. Most reported SH parameters are 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 SH formalism does not generally give improved fits compared with TNM [26] but the SH parameters can be more plausibly linked to possible molecular factors, discussed next.

Consider first the AG parameters s_c^* and $\Delta\mu$ in eq. (4.64). This equation indicates that C and s_c^* are both 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

$$\Delta C_p(T) = C'T_g/T \tag{4.114}$$

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

$$B_{SH} = \frac{N_A s_c^* \Delta\mu}{k_B C' T_g} = \frac{N_A s_c^* \Delta\mu}{k_B T_g \Delta C_p(T_g)} = \frac{N_A \ln(\Omega)\Delta\mu}{T_g \Delta C_p(T_g)}. \tag{4.115}$$

The unit of mass also needs to be defined and for this the concept of a "bead" introduced by Wunderlich and Jones [94] is helpful. Wunderlich defined the bead as 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 inorganic materials 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.

The value of s_c^* is also intuitive and is fraught with uncertainties. The most commonly assumed value is

$$s_c^* = k_B \ln 2 \tag{4.116}$$

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 [95] reversed the logic by equating $\Delta\mu$ with the P – O bond strength and discussed the derived values of s_c^* in terms of the coordination number of phosphates 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. (4.116) is inappropriate for polymers because of constraints imposed by consecutive covalent bonds, and eq. (4.116) was replaced by [96]

$$s_c^* = k_B \ln 2^3 = k_B \ln 8, \tag{4.117}$$

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 no crankshaft motion is assumed then for two adjacent segments

$$s_c^* = k_B \ln 3^2 = k_B \ln 9\,. \tag{4.118}$$

The difference between ln 8 and ln 9 is smaller than any reasonable uncertainty in s_c^*. For large nonpolymeric molecules that are not linear the crankshaft motion is probably irrelevant and it is reasonable to extend eq. (4.118) to

$$s_c^* = k_B \ln 3^{N-1}, \tag{4.119}$$

where N is the number of beads (segments) and N-1 is the number of rotatable bonds between them. Equation (4.119) has not been suggested before and like eq. (4.117) for polymers it has dubious statistical rigor so that values of $\Delta\mu$ derived from it must be regarded as approximate. Because of intra- and inter- molecular geometrical constraints the number of configurations for large molecules is probably less that that given by eq. (4.119) and derived values of $\Delta\mu$ should therefore be regarded as minimum ones.

Hodge and O'Reilly [96] analyzed the SH parameters for five nonpolymeric 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 [96]. Their data are discussed in detail here (more than in the original publication) for two reasons: (i) re-evaluations of s_c^* using eq. (4.119); (ii) revised SH values of $\Delta\mu$ based on these new values of s_c^*. Data from [96] are summarized in Table 4.1 that combines entries in Tables 1 and 4 of [96] as well as results from the new calculations. 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 [96]. The units of $\Delta\mu$ are kJ mol^{-1}, not kJ (mol-bonds)$^{-1}$ as stated in [96]. The boldface $\Delta\mu$ entries correspond to the values of N associated with each material.

TABLE 4.1

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

Inter-segmental rotational energy barriers ΔE are given by the values of $\Delta\mu$ divided by N-1. 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 are 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 beads 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 better). There is an indisputable extrapolation towards $T_g/T_2 \rightarrow 1$ as $B_{SH} \rightarrow 0$ 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 $B \rightarrow 0$ corresponds unambiguously to $\Delta\mu \rightarrow 0$ and suggests that as $\Delta\mu$ approaches zero there is no (average) barrier to prevent T_g approaching some fundamental amorphous state temperature that could be approximated by T_2 and/or T_K ("ideal glass", see §4.2.2.6). This in turn again suggests 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]).

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