1
2 CHAPTER FOUR: STRUCTURAL RELAXATION
3 2/3/2018
4 [FINAL DRAFT]
5

6 ## *Table of Contents*

43

44   4.1   Introduction
45   Structural relaxation refers to changes in the kinetic and thermodynamic properties of
46   nonequilibrium amorphous materials as they approach the amorphous (not crystalline) meta-
47   equilibrium state. It is intimately related to the glass transition phenomenon and glassy state
48   relaxation and a portion of this chapter is accordingly devoted to thermodynamics and the glass
49   transition. There are two significant differences between the kinetics of structural relaxation and
50   the other relaxations considered in earlier chapters. The first is that the underlying phenomena
51   are less well characterized and are often based on extrapolations. They are not understood at
52   anywhere near the level of electrical and visco-elastic relaxations - there are no Maxwell
53   equations nor Newton's laws for succor. This issue essentially arises from the fact that
54   "everything changes with temperature". The second difference is that structural relaxation is
55   strongly nonlinear because the average structural relaxation time depends on the thermodynamic
56   state as well as on temperature – thus the isothermal relaxation time changes as isothermal
57   average relaxation towards thermodynamic equilibrium proceeds. Mathematically this is handled
58   by making the average relaxation time a function of time and replacing the elapsed time with the
59   reduced time defined below.
60   Structural relaxation is most significant within and below the glass transition temperature
61   range that is often but misleadingly referred to as the "glass transition temperature" T_g. Typically
62   T_g is defined as lying within the glass transition temperature range (often but not always
63   midway) and this tradition is followed here until definitions of the glass transition temperature
64   are discussed in §4.8.3.2. Essentially "T_g" will be used as an abbreviation for "glass transition
65   temperature range".
66
67   4.2   Elementary Thermodynamics
68   4.2.1   Nomenclature
69   The SI unit for temperature (Kelvin, symbol K) is used throughout. As usual constant
70   pressure processes are referred to as isobaric, those at constant volume as isochoric, and those at
71   constant temperature as isothermal. The convention that intensive properties such as pressure and
72   temperature are written in lower case and extensive properties such as volume, enthalpy, entropy,
73   heat capacity etc., are written in upper case is *not* followed here, as is often done in textbooks.
74   The principle reasons for this are that an exception must always be made for temperature T to
75   avoid confusion with the time t, and that units indicate the distinction anyway (per kg or per
76   mole for extensive quantities for example). Boltzmann's constant is written as k_B and the ideal
77   gas constant is written as R as is customary. The symbol τ is used for a relaxation time
78   considered as a variable and τ_0 refers to any characteristic relaxation time in expressions such as
79   the nonexponential Williams-Watt (WW) decay function.
80   Thermodynamics is fraught with subtleties that require extensive study to master, so the
81   present exposition is necessarily simplified and abbreviated. Recommended books on the subject
82   include Fermi [1] (terse), Lewis and Randall [2] (aimed at physical chemists), and Landau &
83   Lifshitz [3] (aimed at physicists). Be aware that [3] dispenses with Boltzmann's constant (for
84   good reason, see below) so that T in many of its formulae should be replaced with $k_B T$ to make
85   contact with common usage – this conversion has been made for the formulae from [3] cited
86   below.
87

88   4.2.2   Temperature Scales

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

93   The Celsius and Fahrenheit scales are defined by the melting (T_m) and boiling (T_b)
94   temperatures of water at atmospheric pressure. For the Fahrenheit scale T_m is 32°F and T_b is
95   212°F, the values of which have historical empirical roots: 0°F was originally defined to be the
96   lowest temperature at which water could be frozen when a salt was added, and 100°F was
97   defined to be the temperature of human blood. These values have since been modified to
98   simplify the conversion between the Fahrenheit and more objective Celsius scales. For the
99   Celsius scale T_m is defined to be 0°C and T_b is 100°C. Thus the difference (T_b - T_m) is 100°C
100   compared with 180°F, and after accounting for the 32° difference at the melting temperature of
101   ice the equations for conversion between the Fahrenheit (F) and Celsius (C) scales are

102

103
$$C = (F - 32)/1.80,$$
$$F = 1.80C + 32.$$
           (4.1)

104

105   The temperature at which the two scales are numerically equal is therefore –40°.

106   The ^{o}R and K scales are based on the lowest possible temperature being zero (for the
107   justification of such an absolute zero see any introductory physics or physical chemistry text as
108   [1]–[3]). The absolute Kelvin scale is based on the experimental result that such an absolute zero
109   occurs at –273.15^{o}C and the Rankin scale is based on an absolute zero that occurs at about
110   –459.7^{o}F.

111

112   4.2.3   Quantity of Material

113   The most common metric is the mole whose unit the *mol* equals Avogadro's number
114   $N_A = 6.02 \times 10^{23}$. Even although the mole is a pure number it is useful to keep track of it as if it
115   had the unit *mol* because it is clearly and importantly different from just the number of particles
116   being considered. When using the mole it is important to be aware of the question "mole of
117   what?". For example the gaseous phase of the element sulfur consists of molecules such as S_2,
118   S_4, S_6 and S_8 so that per mole of sulfur is ambiguous.

119

120   4.2.4   Gas Laws and the Zeroth Law of Thermodynamics

121   The ideal gas equation is

122

123   $$PV = nRT = Nk_B T,$$ (4.2)

124

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

129

130 $$\overline{KE} = \frac{3}{2}nRT ,$$ (4.3)

131

132 where $\overline{KE}$ is the average kinetic energy per mole of particles. Equation (4.3) provides a
133 fundamental interpretation of temperature – it is a measure of the average energy of all
134 molecules (for an ideal gas the kinetic energy is entirely translational but in general includes
135 vibrational and rotational degrees of freedom). This equivalence is discussed in detail in [3] and
136 is the reason that k_B is omitted from its equations. A definition of temperature was recognized to
137 be logically necessary well after the 1st and 2nd laws of thermodynamics had been established and
138 the adopted definition is thus referred to as the zeroth law of thermodynamics: "If C is initially in
139 thermal equilibrium with both A and B, then A and B are also in thermal equilibrium with each
140 other. Two systems are in thermal equilibrium if and only if they have the same temperature".
141   Van der Waals improved the ideal gas equation by introducing two corrections:
142 (a)   The finite volume of the particles is subtracted from the volume of the particles to give
143 $(V - nb)$, where b is an empirical constant reflecting the particle volume.
144 (b)   Attractive (van der Waals) forces between the particles reduce the gas pressure because
145 of two factors: (i) because of particle interaction forces the average momentum per particle is
146 reduced in proportion to (n/V), thus reducing the impulsive force per particle arising from each
147 reflection from the walls of the container; (ii) the reduction in total momentum is proportional to
148 the product of the reduction per particle and the number density (n/V) of particles. Thus the
149 pressure is reduced in proportion to (n^2/V^2) and this must be subtracted from P in the ideal gas
150 expression. The result is the Van der Waals equation

151

152 $$(P + an^2/V^2)(V - nb) = RT ,$$ (4.4)

153

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

157

158 $$L = -\left(\frac{3}{4}\right)\frac{h v \alpha^2}{(4\pi e_0)^2 r^6} ,$$ (4.5)

159

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

165

166 4.2.5   Heat, Work and the First Law of Thermodynamics
167   As noted above the temperature of an ideal gas is proportional to the average kinetic
168 energy per ideal gas particle [eq. (4.3)] ("thermal energy"). Heat (Q) is thermal energy in transit

169   that spontaneously flows from a system of higher thermal energy (higher T) to that of lower
170   thermal energy (lower T). The reverse process requires an input of energy (work W) defined by

171

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

173

174   The temperature of any material is a measure of its internal energy U [a generalization of
175   eq. (4.3)] and the balance of heat transfer Q, U and work W is given by the *First Law of*
176   *Thermodynamics*:
177
178    $$U = Q + W$$ (4.7)
179

180   that is valid for all systems. Equation (4.7) adheres to the convention that W is positive for work
181   done *on* the system. An alternative convention regards W as positive for work done *by* the system
182   and the sum on the right hand side of eq. (4.7) then becomes a difference. There is also more to
183   eq. (4.7) than its algebra, because although both Q and W depend on the path taken from one
184   state to the other their sum U is independent of the path. Path invariant functions such as U are
185   often called *state functions*.
186
187   4.2.6   Entropy and the Second Law of Thermodynamics

188   The path dependence of $Q = \int_A^B \delta Q$ is eliminated by dividing all heat transfers δQ by the

189   temperature T at which each transfer occurs. The quantity $\delta Q/T$ is the change in entropy dS and
190   the state function entropy S is given by
191

192    $$S = \int_A^B \frac{\delta Q}{T} = \int_A^B dS.$$ (4.8)

193

194   Entropy is not generally conserved and actually increases for irreversible processes. Consider for
195   example the spontaneous transfer of a quantity of heat Q from a body A at temperature T_A to
196   another body B at a lower temperature T_B. The entropy of the two bodies together increases
197   because the entropy Q/T_A lost by A is smaller than the entropy Q/T_B gained by B. This analysis
198   depends of course on neither heat nor matter (with its internal energy U) entering or leaving the
199   system consisting of $A+B$, and on no work being done on or by the system - the system $A+B$ is
200   then said to be closed or isolated. The *Second Law of Thermodynamics* states that for all
201   processes taking place in a closed system the total change in entropy ΔS is greater than or equal
202   to zero:
203
204    $$\Delta S \geq 0,$$ (4.9)

205

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

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

209

210     $S = k_B \ln \Omega,$ (4.10)

211

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

221 4.2.7   Heat Capacity

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

224

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

225   and   (4.11)

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

226

227   where δQ has been replaced by ∂Q to indicate that the heat transfer is directly into the body and
228 not dependent on path before that. Heat capacities per unit mass are too often referred to as
229 "specific heats" that is confusing and misleading (what prevents the use of "specific heat
230 capacities"?). Heat capacity has the same units as entropy but the two are physically different:
231 entropy is a process dependent quantity related to heat transfer at a particular temperature or a
232 material dependent quantity related to the randomness of the material, whereas heat capacity is a
233 material property that refers to the change in temperature for a given heat input that is
234 independent of the randomness of the material and does not depend on how heat is input to the
235 material.

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

239

240    $$C_P - C_V = \frac{\alpha^2 TV}{\kappa_T} \geq 0 \,,$$ (4.12)

241

242   where
243

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

245

246   is the isobaric expansivity, and
247

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

249

250   is the isothermal compressibility. Mechanical stability demands that $\kappa_T > 0$ so that eq. (4.12)
251   ensures $C_p \geq C_v$ because V and T are positive definite and α^2 is necessarily positive even when
252   α is negative (supercooled water for example). It can be shown [6] that α for solids arises from
253   odd number vibration harmonics (even numbered harmonics do not). The isobaric heat capacity
254   C_p is usually considered in this chapter, an exception being the theoretical Debye heat capacity
255   discussed next.
256

257   4.2.8   Debye Heat Capacity and the Third Law of Thermodynamics
258   Quantum phenomena affect $C_p(T)$ and $C_v(T)$ at low temperatures. Einstein (Chapter 20
259   of [5] entitled "Einstein and Specific Heats") was the first to apply quantum considerations to the
260   heat capacity and thus was the first to deduce that $\lim_{T\to 0} C_v(T) = 0$, although his result that
261    $\lim_{T\to 0} C_v(T) \propto T$ is quantitatively incorrect. Debye extended Einstein's result by introducing a
262   distribution of phonon (collective vibrational quanta) energies rather than Einstein's heuristic
263   assumption of a single energy. The Debye result for N oscillators is [6]
264

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

266
267   where Θ_D is the Debye temperature corresponding to a maximum cutoff energy for the
268   distribution of phonon (vibrational quanta) energies and $x_D = \theta_D / T$. For $T \to 0$ the parameter x_D
269    $\to \infty$ 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
270   behavior is observed for crystalline materials but not for many glasses for which $\lim_{T\to 0} C_V(T) \propto T$.

271   The latter has been rationalized in terms of two state models [6] but is not understood at a
272   fundamental level because the two states are unknown. In both cases however it remains true that

273    $\lim_{T\to 0} C_v(T) = 0$ 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

274   implies that $\Omega = 1$ and there is only one possible state at 0 K. This is the basis of the *Third Law*
275   *of Thermodynamics* (originally called the Nernst Theorem), one of the best expressions of which
276   is probably that due to Fermi [1]:

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

280   Immediately after that definition Fermi adds an important comment:

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

287   Some sort of "ideal glass" with an energy degenerate number of configurations much fewer than
288    $\exp(N)$ at 0 K is perhaps a candidate for a "not theoretically impossible" state. Also, a peak in
289   the low temperature glassy heat capacity is sometimes observed in excess of the Debye T^3
290   behavior, known as the boson peak. Its origins are not yet understood but it is known to change
291   with thermal history including annealing. Its occurrence points to low energy excitations that
292   may also be candidates for the "not theoretically impossible states" mentioned by Fermi.
293

294   4.3   Thermodynamic Functions
295   4.3.1   Entropy *S*
296

297    $dS = \dfrac{\delta Q}{T}$.   (4.16)

298

299   As with eq. (4.7) there is more to equation (4.16) than just the algebra. The use of δQ rather than

300   dQ indicates that as noted in §4.2.2.4 the total heat $\int_A^B \delta Q$ transferred to or from the system from

301   state *A* to state *B* is path dependent, but dS is used for entropy because the total entropy change

302    $\Delta S = \int_A^B dS$ is not path dependent.

303

304   4.3.2   Internal Energy *U*
305   This is defined by eq. (4.7). In terms of the other thermodynamic functions defined here:
306

307    $dU = TdS - PdV$.   (4.17)

308

309   **4.3.3   Enthalpy *H***
310   Defined as
311

$$H = U + PV;$$
312 $$dH = (TdS - PdV) + (VdP + PdV) \tag{4.18}$$
$$= TdS + VdP.$$

313

314   **4.3.4   Free Energies *A* and *G***
315   Free energies are thermodynamic potentials (defined as such in [3]) because systems are
316   driven to decrease their free energies. The Helmholtz free energy *A* and Gibbs free energy *G*
317   correspond to isochoric and isobaric conditions respectively:
318

$$A = U - TS,$$
319 $$\tag{4.19}$$
$$dA = -PdV - SdT,$$

320

$$G = H - TS = U + PV - S$$
321 $$\tag{4.20}$$
$$dG = VdP - SdT.$$

322

323   The negative sign of the *TS* term in eqs. (4.19) and (4.20) signifies that systems are in part driven
324   to equilibrium by increasing their entropy. The other term signifies that systems are also driven
325   to decrease their energy *U* or *H*. It is the balance of these potentially conflicting drives that
326   defines the eventual direction of a process or reaction, as illustrated by the thermodynamics of
327   DNA helix formation: it is energetically favored by hydrogen bonding between bases but
328   entropically expensive because it is more ordered compared with the disorder of separated
329   strands and more disordered ambient water molecules. The coding and decoding of DNA at
330   room temperature therefore depends on the small difference between large enthalpy and entropy
331   factors.
332

333   **4.3.5   Chemical Potential μ**
334   For a species *i* this quantity is denoted by μ_i and is needed when there are a number of
335   different entities in a system. If this number is n_i for species *i* then [3]
336

337 $$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V} = \left(\frac{\partial W}{\partial n_i}\right)_{S,P}. \tag{4.21}$$

338
339   Which derivative is chosen depends on the variables in which μ_i is to be expressed – for example
340   if *G* is chosen the variables are {*P*, *T*} and if *A* is chosen the variables are {*V*, *T*}. The entities
341   can be atoms, molecules, ions, even electrons. For charged entities the electrostatic potential
342    $z_i e\varphi$ must be added to μ_i to give the electrochemical potential μ_i^E
343

344 $$\mu_i^E = \mu_i + z_i e\varphi \tag{4.22}$$

345

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

348

349 **4.3.6 Internal Pressure**
350 Defined as $T\left(\partial S / \partial V\right)_T$ and motivated by

351

352 $$dU = -PdV + TdS \Rightarrow \left.\frac{\partial U}{\partial V}\right|_T = -P + T\left(\frac{\partial S}{\partial V}\right)_T.$$ (4.23)

353

354 **4.3.7 Derivative Properties**
355 Properties that are defined in terms of the first or second derivatives of free energy with
356 respect to temperature, pressure or volume are often referred to as first or second order functions.
357 For example

358

359 $$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T,$$ (4.24)

360

361 $$P = -\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T,$$ (4.25)

362

363 and

364

365 $$S = -\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P$$ (4.26)

366

367 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
368 order functions. In addition to eq. (4.12) the difference between C_p and C_V is also given by

369

370 $$C_P - C_V = \left.\left(\frac{\partial H}{\partial T}\right)\right|_P - C_V = \left.\left(\frac{\partial U}{\partial T}\right)\right|_P + \left.\left(\frac{\partial (PV)}{\partial T}\right)\right|_P - C_V.$$ (4.27)

371

372 4.4   Maxwell Relations
373   The Maxwell relations relate the derivatives of various thermodynamic functions. For
374 example
375

376 $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V,$$ (4.28)

377

378 $$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \Leftrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,$$ (4.29)

379

380 $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.$$ (4.30)

381

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

383 $$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right),$$ (4.31)

384

385 obtained from
386

387 $$C_p = T\left(\frac{\partial S}{\partial T}\right)_T \Rightarrow \left(\frac{\partial C_p}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial P \partial T}\right)$$ (4.32)

388

389 so that

390

391 $$\left(\frac{\partial S}{\partial P}\right)\Big|_T = -\left(\frac{\partial V}{\partial T}\right)\Big|_P \Rightarrow \left(\frac{\partial^2 S}{\partial P \partial T}\right) = -\left(\frac{\partial^2 V}{\partial T^2}\right)\Big|_P.$$ (4.33)

392

393 Another example is [2]
394

395 $$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P.$$ (4.34)

396

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

399 4.5   Fluctuations
400   Thermodynamic functions F are defined by averages $\langle F \rangle$ over large numbers of entities.

401 These averages have corresponding variances $\langle F^2 \rangle$ and standard deviations $\langle F^2 \rangle^{1/2}$ that are

402 referred to as "fluctuations". These fluctuations are sometimes related to thermodynamic
403 functions. For example [3]
404

405   $k_B C_p = \langle \Delta S^2 \rangle$ (4.35)

406

407 and

408

409   $k_B T V \kappa = \langle \Delta V^2 \rangle .$ (4.36)

410

411 4.6   Egodicity and the Deborah Number
412   Egodicity is a statement about the equivalence of probabilities in terms of time averages
413 and various ensemble averages in statistical mechanics. The ensembles are distinguished by their
414 variables: canonical (n, V, T), micro-canonical (n, V, U), and grand canonical (μ, V, T). The
415 essence of ergodicity is illustrated by a simplified traffic analogy. For the analogy to be good it is
416 required to assume that all drivers on the road behave the same (much less likely than assuming
417 all molecules act alike). Consider the probability of a driver doing something such as turning
418 with no turn signal to indicate intent ("event" hereafter). There are two ways to evaluate the
419 probability that such an event will occur:
420 (i)   Observe traffic behavior in a restricted area (a county say) for a "very long time" and find
421 the probability that the event occurs. A "very long time" can be defined as the minimum
422 observation time for which longer observation times would not change the probability.
423 (ii)   Observe all traffic patterns over the country for an "instant" and average them to obtain
424 the probability of no turn signals.
425   The ergodic hypothesis asserts that these two probabilities are the same. However if the
426 time of observation in (i) is too short to include all possibilities then ergodicity is said to be
427 broken and the time average will be incorrect. This occurs in the glassy state where relaxation
428 times of years or even millennia are confidently estimated and longer observation times are
429 impractical. The glass transition phenomenon is correctly said to be "ergodicity breaking" but it
430 is incorrect to assert that ergodicity breaking is equivalent to a glass transition (see discussion of
431 the Deborah Number below and the article by Angell [7]). Such assertions ignore the details and
432 subtleties of the glass transition phenomenon.
433   A rigorous discussion of ergodicity is given in [5] (Chapter Four "Entropy and
434 Probability") from which the following is distilled. Two definitions by Boltzmann are discussed.
435 The first, dating from 1868, considers the evolution in time of a closed system of N particles in
436 orbit on a surface of constant energy in $6N$-dimensional space. A particular state S_i then
437 corresponds to a point i on the orbit. Now observe the system for a long time T and determine the

438   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

439   S_i. Einstein independently introduced the same definition in 1903 and was his favored definition.

440   Boltzmann's second definition was to calculate the number of ways w of partitioning n_i particles

441   each with energy ε_i under the constraints that the total energy $E = \sum n_i \varepsilon_i$ and $N = \sum n_i$ are

442   fixed and (crucially) that the particles are in practice distinguishable (not so quantum

443   mechanically). Boltzmann then proposed that w was proportional to the probability of any

444   distribution of $\{n_i\}$ values. The first definition is in principle observable but the second is, in

445   Pais's words [5], "more like a declaration". Ergodicity asserts that Boltzmann's two definitions

446   are equivalent but as Pais has stated "This [equivalence] is the profound and not yet fully solved

447   problem of ergodic theory".

448   The Deborah number DN [8] is defined as the ratio of the characteristic timescale of the

449   observed system (typically a relaxation time) and of the measurement timescale. For an applied

450   sinusoidal perturbation an appropriate timescale of observation is the period of oscillation. The

451   glass transition occurs when the DN passes through unity with changing temperature – for

452   example during rate cooling through the glass transition temperature range (abbreviated by "T_g"

453   as noted in §4.1). Above T_g relaxation times are less than about 100 s and longer observation

454   times are easily achieved. Relaxation times of years or even millennia are confidently estimated

455   below T_g so observation times are then necessarily much smaller. The DN is also usefully

456   defined as [8]

457

458    $$DN \equiv \frac{d\tau}{dt} = \left(\frac{d\tau}{dT} \right) \left(\frac{dT}{dt} \right) = \left(\frac{d\tau}{dT} \right) Q_c \, , \qquad\qquad (4.37)$$

459

460   where Q_c is the cooling rate (the heating rate is not recommended because for DSC scans the

461   kinetics of recovery are partly determined by the previous thermal history (see [8] for details).

462

463   4.7   Phase Transitions

464   These are transitions between different states (phases) of a material (e.g liquid and solid).

465   A useful classification scheme for them was introduced by Ehrenfest who proposed that

466   discontinuous changes in a property defined by the nth derivative of a thermodynamic potential

467   (free energy A or G) be termed an nth order transition. Thus melting and boiling for which first

468   order properties such as V, H and S are discontinuous are 1st order transitions. Transitions for

469   which second order properties such as the heat capacity C_p or C_v, expansivity α, or

470   compressibility κ are discontinuous are 2nd order transitions, and so on. The Ehrenfest

471   classification is imperfect – for example λ transitions in metal alloys are referred to as second

472   order transitions but do not fall into Ehrenfest's classification (but could perhaps be

473   approximated as Ehrenfest third order transitions). In any event it is useful to discuss the glass

474   transition phenomenon in terms of an Ehrenfest 2nd order transition.

475   If the glass transition is regarded as an Ehrenfest 2nd order transition then its pressure

476   dependence can be derived for different thermodynamic functions that are used to define the

477   glass transition, using elementary calculus. These thermodynamic relations are applied both

478   below and above the transition temperature range and the difference between them is denoted by

479   Δ. Thus $\Delta V = \Delta H = \Delta S = 0$ because the transition is not first order but their first derivatives are

480   not zero because by definition an Ehrenfest 2nd order transition exhibits discontinuities in these
481   derivatives.

482   For volume

483

484
$$d\Delta V = 0 = \left(\frac{\partial \Delta V}{\partial T}\right)_P dT + \left(\frac{\partial \Delta V}{\partial P}\right)_T dP = V\left(\Delta \alpha \, dT - \Delta \kappa_T \, dP\right) \qquad (4.38)$$

485

486   from which

487

488
$$\left(\frac{\partial T_2}{\partial P}\right)_V = \frac{\Delta \kappa_T}{\Delta \alpha}, \qquad (4.39)$$

489

490   where eqs. (4.13) and (4.14) for $\Delta\alpha$ and $\Delta\kappa_T$ have been used. Deviations from eq. (4.39) have
491   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
492   strongly pressure dependent and that reasonable values can be found for it that agree with eq.
493   (4.39).

494   For enthalpy

495

496
$$d\Delta H = \left(\frac{\partial \Delta H}{\partial T}\right)_P dT + \left(\frac{\partial \Delta H}{\partial P}\right)_T dP = \Delta C_p \, dT + \left[\Delta V - T\left(\frac{\partial \Delta V}{\partial T}\right)_P\right] dP = 0 \qquad (4.40)$$

497

498   but since $\Delta V = 0$ then

499

500
$$\left(\frac{\partial T_2}{\partial P}\right)_H = VT\frac{\Delta \alpha}{\Delta C_p}. \qquad (4.41)$$

501

502   For entropy

503

504
$$d\left(\Delta S\right) = 0 = \left(\frac{\partial \Delta S}{\partial T}\right)_P dT + \left(\frac{\partial \Delta S}{\partial P}\right)_T dP = \left(\frac{\partial \Delta S}{\partial T}\right)_P dT - \left(\frac{\partial \Delta V}{\partial T}\right)_T dP$$
$$= T^{-1}\Delta C_p \, dT - V\Delta \alpha \, dP \qquad (4.42)$$

505

506   so that

507

508 $$\left(\frac{\partial T}{\partial P}\right)_{\Delta S} = VT\frac{\Delta\alpha}{\Delta C_p}.$$ (4.43)

509

510 Note that eqs. (4.41) and (4.43) are the same.

511   In anticipation of the nonlinear Adam-Gibbs model for structural relaxation discussed in
512 §4.8.3, an expression for $\partial T_2 / \partial P$ based on TS_c being constant is now given. The condition that
513 TS_c be constant implies

514

515 $$\begin{aligned} d\left(TS_c\right) &= TdS_c + S_c dT = 0 \\ &= \Delta C_p dT - TV\Delta\alpha dP + S_c dT \\ &= \left(\Delta C_p + S_c\right)dT - TV\Delta\alpha dP \end{aligned}$$ (4.44)

516
517 so that
518

519 $$\left(\frac{\partial T_2}{\partial P}\right)_{TS_c} = VT\frac{\Delta\alpha}{\Delta C_p + S_c}.$$ (4.45)

520

521   The Prigogine-Defay ratio Π is defined by

522

523 $$\Pi \equiv \frac{\left(\partial T_2 / \partial P\right)\big|_{\Delta V}}{\left(\partial T_2 / \partial P\right)\big|_{\Delta S}} = \frac{\Delta C_p \Delta\kappa_T}{TV\left(\Delta\alpha\right)^2}.$$ (4.46)

524

525 It has been shown by Davies and Jones [10] that if $\Pi > 1$ then more than one thermodynamic
526 variable must determine the transition. Values of $\Pi > 1$ for $T_2 = T_g$ have often been reported but
527 McKenna [11] has suggested that the usually quoted values of $\Delta\alpha$, $\Delta\kappa_T$ and ΔC_p are not obtained
528 under the proper conditions and that if they were then Π could be unity within uncertainties. If
529 one variable is chosen for convenience to determine relaxation behavior then entropy is evidently
530 better than volume because entropy and enthalpy can accommodate things that volume cannot,
531 such as bond angle constraints and stresses that are known to affect glassy state relaxation rates
532 and are presumably factors in liquid relaxation as well.

533 4.8   Structural Relaxation
534   An excellent account of this topic is given by Angell et al. [12] that lists questions that
535 need answering and the then current best answers (essentially unchanged to this day). It also
536 considers other topics such as ionic conductivity in glasses that are discussed in Chapter Two of
537 this book. The present section is divided into three segments arranged according to three

538   temperature ranges relative to T_g: (1) $T > T_g$ (supercooled liquids); (2) $T < T_g$ (glasses); (3) $T \approx$
539   T_g (glass transition).

540   4.8.1 Supercooled Liquids and Fragility
541   Supercooled liquids are precursors to glasses formed by cooling through the glass
542   transition temperature range and their properties are therefore relevant to structural relaxation.
543   Relaxation times in supercooled liquids (as well as many liquids above the melting temperature)
544   rarely conform to the Arrhenius temperature dependence
545

546    $$\tau_0(T) = A_A \exp\left(\frac{E_a}{RT}\right), \qquad (4.47)$$

547

548   where E_a is the Arrhenius activation energy and A_A is a constant. Instead they generally adhere to
549   relations that are often well approximated by the Fulcher equation (see [13] for an excellent
550   discussion of its history and [14] for a reprint of the original paper):
551

552    $$\tau_0(T) = A_F \exp\left(\frac{B_F}{T - T_0}\right), \qquad (4.48)$$

553

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

556

557    $$\left(\frac{E_{eff}}{R}\right) \equiv \left[\frac{d \ln \tau_0}{d(1/T)}\right] = \left[\frac{B_F}{\left(1 - T_0/T\right)^2}\right]. \qquad (4.49)$$

558

559   Other expressions for $\tau_0(T)$ are discussed in [12] but we select just one here for further
560   discussion because it is frequently used in the polymer community – the WLF equation:
561

562    $$\log_{10} a_T \equiv \log_{10}\left[\frac{\tau(T)}{\tau(T^*)}\right] = \frac{C_1(T - T^*)}{\left[T - (T^* - C_2)\right]}, \qquad (4.50)$$

563

564   where T^* is a reference temperature that is usually equated to the glass transition temperature T_g
565   and C_1 and C_2 are "constants" (that depend on T^* however). The parameters C_1 and C_2 are
566   related to the Fulcher parameters B_F and T_0 by
567

568    $$T_0 = T^* - C_2 \qquad (4.51)$$

569

570   and

571

572    $$B_F = 2.303 C_1 C_2, \qquad (4.52)$$

573
574 where the factor 2.303 arises from the irritating use of $\log_{10}$ rather the natural ln. Equations
575 (4.51) and (4.52) indicate why C_1 and C_2 are T^* dependent: T_0 is an objective measure of
576 departure from Arrhenius behavior [eq. (4.49)]. The value of C_1 for $T^* = T_g$ is "universally"
577 about 17 for polymers but C_2 is material dependent.

578   A fruitful characterization of supercooled liquids is the classification scheme of fragility
579 introduced by Angell. This scheme has been developed over many publications and is not
580 amenable to a definitive citation (although [15,16] are useful and [17] includes a list of
581 references). Reference [17] criticizes some mathematical issues related to fragility but these
582 criticisms do not detract from the overall value of the concept.

583   There are two complementary definitions of fragility, thermodynamic and kinetic, that
584 reflect the intricate and debated relation between the thermodynamic and kinetic aspects of the
585 glass transition phenomenon (such a relation is the basis of the Adam-Gibbs model [18]
586 discussed below). The thermodynamic definition is the origin of the term fragility and defines it
587 in terms of the isobaric heat capacity change $\Delta C_p\left(T_g\right)$ over the glass transition temperature
588 range: large values of $\Delta C_p\left(T_g\right)$ imply large increases in the configurational entropy with
589 increasing temperature above T_g, that in turn implies large decreases in structural order and
590 therefore a more fragile structure. The kinetic definition of fragility is essentially a quantitative
591 statement of the generally observed positive correlation between $\Delta C_p\left(T_g\right)$ and the departure
592 from Arrhenius behavior of $\tau_0\left(T\right)$, the latter often being well described by the Fulcher equation.
593 The kinetic definition was originally expressed in terms of the Fulcher equation but it has since
594 been more generally defined in terms of a fragility parameter m that is essentially a T_g-scaled
595 effective Arrhenius activation energy at T_g that is independent of the form of $\tau_0\left(T\right)$:

596

597 $$m \equiv \left.\frac{d\log_{10}\left(\tau_0\right)}{d\left(T_g/T\right)}\right|_{T=T_g} = \frac{E_{eff}}{RT_g} \; . \tag{4.53}$$

598

599 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
600 values of τ_0 are determined by the plausible boundary conditions $\tau_0 = 10^2$ s at $T \approx T_g\left(T_g/T \approx 1\right)$
601 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
602 fragility index is obtained from the slope of the Angell plot obtained by connecting the two
603 limiting values of τ_0 with a straight (Arrhenius) line. For the boundary conditions given above

604

605 $$m_{min} = \log_{10}\left[\frac{\tau_0\left(T_g\right)}{A_A}\right] = 2-\left(-14\right) = 16 \; . \tag{4.54}$$

606

607 The quantity A_A in eq. (4.54) refers specifically to the Arrhenius equation (4.47), and not to any
608 other equation for $\tau_0\left(T\right)$ that has a pre-exponential factor (A_F in eq. (4.48) for example) that is

609   too often just termed A in the literature and can be confused with A_A. To ensure that the argument
610   of the logarithm function is explicitly dimensionless the following modified form is useful:
611

612    $$m' \equiv \frac{d \log_{10}(\tau_0 / A_A)}{d(T_g / T)}\Bigg|_{T=T_g} \qquad \left(0 \leq T_g / T \leq 1\right) . \tag{4.55}$$

613

614   Equation (4.55) provides a mathematically direct derivation of m_{min} by simply demanding that
615   the derivative in eq. (4.55) be independent of temperature. Angell [19] has described how m_{min}
616   predicts the "universal" WLF parameter $C_1 \approx 17$.
617   The thermodynamic and kinetic definitions of fragility are equivalent according to the
618   Adam-Gibbs (AG) [18] model for liquid state transport properties. This model gives rise to
619   equations that are almost indistinguishable from the Fulcher equation in many cases
620   and for $\Delta C_p(T) = C / T$ (see below) it reproduces the Fulcher equation exactly. The
621   ease with which this equation can be extended through the glass transition to the glassy
622   state was quickly recognized by Macedo and Napolitano [20], Goldstein [21], Plazek
623   and Magill [22], Magill [23], and Howell et al. [24], but was not used explicitly for enthalpy
624   relaxation until the pioneering work of Scherer [25] and in later studies by Hodge [26].
625   The AG model is based on transition state theory and the hypothesis that a
626   temperature dependent number of moieties need to rearrange cooperatively for relaxation
627   to occur. The transition state activation energy E_A is approximated by
628

629    $$E_A = z\Delta\mu, \tag{4.56}$$

630

631   where $\Delta\mu$ is an elementary excitation energy per moiety and z is the number of moieties
632   that cooperatively rearrange. The linear addition of $\Delta\mu$ for each moiety implicitly
633   assumes that the moieties do not interact and this has been challenged by Ngai et al.
634   who have proposed an alternative "coupling model" [27]. Only the minimum value z^* of z
635   significantly contributes to the relaxation time [18] and its value is assumed to be a
636   function of temperature derived by simplistically equating two expressions for the
637   configurational entropy per moiety
638

639    $$\frac{S_c(T)}{N_A} = \frac{s_c^*}{z^*(T)}, \tag{4.57}$$

640

641   where $S_c(T)$ is the macroscopic configurational entropy (defined in eq. (4.59)
642   below), N_A is Avogadro's number, and s_c^* is the configurational entropy associated with the
643   smallest number of particles capable of rearranging (often taken to be $k_B \ln 2$ because of the
644   two configurations before and after rearrangement). Thus
645

646 $$\tau_0 = A\exp\left(\frac{E_A}{RT}\right) = A_{AG}\exp\left(\frac{z*(T)\Delta\mu}{k_B T}\right) = A_{AG}\exp\left(\frac{N_A s_c^* \Delta\mu}{k_B T S_c(T)}\right),$$ (4.58)

647

648 where a pre-exponential factor $\left[1-\exp\left(-\Delta\mu/k_B T\right)\right]^{-1}$ has been equated to unity

649 because typically $\Delta\mu \gg k_B T$. The result that configurational entropy is the fundamental

650 property that determines the rate of relaxation is plausible because if more

651 configurations are available then relaxation can be expected to be faster.

652   The quantity $S_c(T)$ is given by

653

654 $$S_c(T) = \int_{T_2}^{T} \frac{\Delta C_p(T')}{T'} dT' = \int_{\ln T_2}^{\ln T} \Delta C_p(T') d\ln T',$$ (4.59)

655

656 where (i) $\Delta C_p(T) \equiv C_{pe}(T) - C_{pg}(T)$ and $C_{pe}(T)$ and $C_{pg}(T)$ are the equilibrium

657 (liquid) and glassy heat capacities respectively; (ii) T_2 is the temperature at which

658 $S_c(T)$ is zero, denoted as such to distinguish it from the thermodynamic Kauzmann

659 temperature T_K discussed below (their possible equality needs to be established

660 experimentally rather than simply asserted). Assessment of $\Delta C_p(T)$ is not trivial. It

661 must be obtained by extrapolations of $C_p(T)$ that are necessarily uncertain in part

662 because the glassy heat capacity $C_{pg}(T)$ must be obtained at temperatures well

663 below T_g to ensure that relaxation effects are not included in its temperature

664 dependence, so that long extrapolations are required. Huang and Gupta [28] have

665 evaluated expressions for $C_{pg}(T)$ suitable for extrapolation into and above the glass

666 transition temperature range for a soda lime silicate glass. The function $\Delta C_p(T)$ also

667 depends on how C_{pl} is extrapolated. It is common to assume that $\Delta C_p(T_g)$ is totally

668 configurational but this has been challenged by Goldstein [29,30] who has argued

669 that it may contain significant contributions from vibrational and secondary relaxation

670 sources. It is however possible that such non-configurational contributions to $\Delta C_p(T)$ could

671 also contribute to "S_c" in the AG model so that using $\Delta C_p(T)$ regardless of its origin could still

672 be valid. The default position adopted here is that indeed all the contributions to $\Delta C_p(T_g)$ of

673 whatever type contribute to structural relaxation.

674   The AG function for $\tau_0(T)$ depends on the functional form of

675 $\Delta C_p(T)$. For

676

677 $$\Delta C_p = C = \text{constant}$$ (4.60)

678

679 the "AGL" function for the structural relaxation time is

680

681 $$\tau_0(T) = A_{AGL} \exp\left[\frac{B_{AGL}}{T \ln(T/T_2)}\right] \qquad (4.61)$$

682
683 where
684

685 $$B_{AGL} = \frac{N_A s_c^* \Delta\mu}{k_B C}. \qquad (4.62)$$

686
687 Equation (4.61) is almost indistinguishable from the Fulcher equation and in fact
688 retaining only the first term in the expansion of the logarithmic term reproduces the
689 Fulcher form. The expression
690

691 $$\Delta C_p(T) = C'T_g/T \qquad (4.63)$$

692
693 implies
694

695 $$S_c(T) = \Delta C(T_g)T_g[1 - T_2/T]/T_2 \qquad (4.64)$$

696
697 so that
698

699 $$\tau_0(T) = A_{AG} \exp\left[\frac{B_{AG}}{T(1 - T_2/T)}\right] = A_{AG} \exp\left[\frac{B_{AG}}{T - T_2}\right], \qquad (4.65)$$

700
701 i.e. the Fulcher form is recovered with
702

703 $$B_F = \frac{N_A s_c^* \Delta\mu T_2}{k_B T_g \Delta C_p(T_g)}. \qquad (4.66)$$

704
705 As noted in [8] eq. (4.63) has a stronger temperature dependence than that observed
706 for most polymers, according to plots of the data compiled in [31]. However since eqs.
707 (4.61) and (4.65) are almost indistinguishable the AG model can probably accommodate most
708 approximations to the Fulcher equation that are found experimentally [32,33].

709   Equations (4.57) and (4.64) imply that z^* is proportional to $1/(1 - T_2/T)$. Thus
710 z^* and the barrier height $z^*\Delta\mu$ diverge as $T \to T_2$ and simplistically this divergence
711 can be expected to prevent T_g approaching T_2 [26,34], (assuming that T_2 is indeed some
712 sort of ideal T_g). Since z^* is conceivably associated with some form of correlation length
713 it is of interest that the correlation length computed from a random field Ising model also
714 diverges as $(1 - T_c/T)^{-\gamma}$ [35], although no evidence for a correlation length was

715 observed in a viscosity study of glycerol by Dixon et al. [36] nor in a molecular
716 dynamics simulation by Ernst et al. [37]. On the other hand if z^* is interpreted in
717 dynamic terms, for example as the minimum number of particles needed for the
718 ensemble averaged time correlation function to be independent of size, it would not
719 necessarily be seen structurally ("dynamic heterogeneity"). It is also possible that z^*
720 corresponds in some way to the "dynamic characteristic length" defined by the ratio of
721 the frequency of the Raman "boson" peak to the speed of sound [38,39]. Adam-Gibbs
722 behavior has been observed in a spin facilitated kinetic Ising model described by
723 Frederickson [40] and as noted above the AG equation has also been extended through the
724 glass transition to the glassy state (discussed in §4.8.3).

725   The assertion made above that the kinetic and thermodynamic definitions of
726 fragility are made physically consistent by the AG model can now be explained. Since S_c
727 is more strongly temperature dependent for greater $\Delta C_p(T_g)$ (greater thermodynamic
728 fragility) eq. (4.58) indicates that the structural relaxation time has a more non-Arrhenius
729 temperature dependence and larger m [eq. (4.53)] (greater kinetic fragility).

730

731 4.8.2 Glassy State Relaxation

732   Because glasses are usually in a nonequilibrium state they isothermally relax
733 towards the equilibrium state (metastable with respect to the crystalline phase however). A
734 discussion of this phenomenon has been given elsewhere [8]. There are two canonical
735 aspects of glassy state relaxation kinetics that need to be considered – nonexponentiality
736 and nonlinearity. The former is a characteristic of relaxation in essentially all condensed
737 media (water is an exception as usual) and has been discussed extensively in Chapter 1.
738 Nonlinearity is absent for most relaxation phenomena, but for structural relaxation
739 nonlinearity cannot be ignored for even small perturbations. It is responsible for several
740 observed phenomena, such as glassy state relaxation occurring on human lifetime scales
741 rather on inhuman scales of centuries or longer [41] for example. Experimental evidence
742 for nonlinearity in glassy state relaxation is exemplified by the creep data of Struik [42]
743 that are reproduced in [41]. Creep is essentially a quantitative measure of the fractional
744 increase in length with time of a vertically suspended small diameter thread of material
745 that has a hanging weight on it. The Struik data were recorded for time intervals that were
746 about 10% of the annealing times t_a. The creep curves moved to longer times with
747 increasing t_a but the shape of each creep curve was essentially the same for all t_a - thus the
748 characteristic relaxation time increased with t_a. A good description of the increase in
749 relaxation time τ_0 with t_a was given by the Struik relation

750

751 $$\tau_0 = Kt_a^{\mu}, \tag{4.67}$$

752

753 where K has the dimensions of $t^{1-\mu}$ and is dependent on material and annealing
754 temperature. The quantity $0 \le \mu \le 1$ is an empirical parameter referred to here as the Struik
755 shift parameter. The nonlinearity of relaxation expressions that contain eq. (4.67) (and
756 other relations that are discussed below) is eliminated by the reduced time defined by
757 [43,44]
758

759 $$\xi(t) \equiv \int_{-\infty}^{t} \frac{dt'}{\tau(t')},$$ (4.68)

760

761 so that for $\tau(t') = \tau_0^{1-\mu} t'^{\mu}_a$

762

763 $$\xi(t) = \frac{(t/\tau_0)^{(1-\mu)}}{(1-\mu)} \qquad \left[\xi(-\infty) = 0\right].$$ (4.69)

764

765 For example the nonlinear WW function is [8]

766 $$\exp\left\{-\left[\xi(t)\right]^{\beta}\right\} = \exp\left\{-\left[\frac{(t/\tau_0)^{(1-\mu)}}{(1-\mu)}\right]^{\beta}\right\} = \exp\left\{-\left[\frac{t^{(1-\mu)\beta}}{(1-\mu)\tau_0^{1-\mu}}\right]\right\} = \exp\left[-\left(\frac{t}{\tau_0'}\right)^{\beta'}\right]$$ (4.70)

767

768 where

769

770 $$\beta' = 1 - \beta$$ (4.71)

771

772 and

773

774 $$\tau_0' = \tau_0 (1-\mu)^{1/(1-\mu)}.$$ (4.72)

775

776 The mathematical equivalence of the linear and nonlinear WW equations exhibited in eq.
777 (4.70) has engendered many published analyses that are physically unreasonable because
778 in the name of "simplicity" they invoke the linear WW equation in situations that demand
779 the consideration of nonlinearity, such as glassy state relaxation for which the Struik
780 relation eq. (4.67) was originally observed experimentally. Some of these incorrect
781 analyses are cited as refs. 53-60 in [8].

782 Quantification of nonlinearity for temperature dependent phenomena is simplified
783 by defining a good metric for the nonequilibrium state. The fictive temperature T_f
784 introduced by Tool [45-47] is such a metric. It was originally suggested in an oral
785 presentation in 1924, so that nonlinearity was recognized as being important to structural
786 relaxation well before nonexponentiality was. Ironically Tool's analysis was for silicate
787 glasses that are now known to have some of the least nonlinear structural relaxation
788 kinetics. Qualitatively T_f is the temperature at which some nonequilibrium property
789 (volume, enthalpy, entropy, relative permittivity, etc.) of a material would be the
790 equilibrium one, and is typically different for different properties of the same sample of
791 material. Since T_f can be associated with any property the phenomenologies described

792 below can be applied to any property. For enthalpy H, whose relaxation phenomenology is
793 representative of all properties, T_f is defined by

794

795 $$H(T) = H_e(T_f) - \int_T^{T_f} C_{pg}(T')dT',$$ (4.73)

796

797 where $H_e(T_f)$ is the equilibrium value of H at T_f and $C_{pg}(T')$ is the temperature dependent
798 isobaric heat capacity of the glass. Equation (4.73) is illustrated in [8] and its temperature
799 derivative is (using eq. 1.18)

800

801 $$\frac{dT_f}{dT} = \frac{(C_p - C_{pg})\big|_T}{(C_{pe} - C_{pg})\big|_{T_f}} \approx \frac{(C_p - C_{pg})\big|_T}{(C_{pe} - C_{pg})\big|_T} \equiv C_p^N,$$ (4.74)

802

803 where $g(T_g) = (1 - T_2/T_g)^{-1} \approx x^{-1}$ is the normalized heat capacity. It is often assumed that
804 $df/d(1/T)\big|_{T_g}$ but this is unjustified in general [48,49(Sindee Simon)].

805   For polymers nonthermal perturbations such as mechanical stresses (shear and
806 tensile), hydrostatic pressure, and vapor induced swelling followed by rapid desorption,
807 all decrease the average isothermal structural relaxation time in the glasses. Accounts of
808 these effects are given in [8,50,51] that include many references to original publications
809 on the effects of nonthermal perturbations on enthalpy relaxation in particular.
810 Applications of the TNM phenomenology to these histories [50] often approximate
811 applied stresses and pressure as isothermal changes in fictive temperature. An instructive
812 example is the formation of "pressure densified polystyrene" by cooling the sample
813 through the glass transition temperature range under hydrostatic pressure and then
814 releasing the pressure in the glassy state (typically at room temperature). The resultant
815 glass has a higher density and enthalpy than that prepared by cooling under ambient
816 pressure and has a shorter structural relaxation time. The fact that relaxation is faster at a
817 smaller volume is inconsistent with the free volume models frequently used by polymer
818 physicists [52] but is consistent with enthalpy/entropy models such as Adam-Gibbs.

819
820 4.8.3 The Glass Transition
821 4.8.3.1 Introduction

822   This vast subject is the focus of two excellent books by Donth [53,54] and at least
823 three reviews [7,8,41], and its applications to material science have been well described
824 by Scherer [55]. This section mainly considers the relaxation aspects of the glass
825 transition phenomenon, although a brief general overview of it is given to provide a
826 context for the relaxation phenomenology. In particular the intricate and still debated link

827 between thermodynamics and kinetics for the observed glass transition phenomenon is
828 discussed.

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

836
837 4.8.3.2 Glass Transition Temperature

838   The phrase "glass transition temperature" is a misnomer because, as noted above
839 (§4.8.1), the transition from a liquid (relaxation time << observation time) to a glass
840 (relaxation time >> observation time) during cooling and heating occurs over a range of
841 temperature. Thus the glass "transition" is not a transition in the traditional sense but
842 rather a phenomenon that in many cases occurs over an unexpected and thus far
843 theoretically unexplained narrow temperature range. Nonetheless an ASTM publication
844 [57] compiles several contributions to a session on definitions of the glass transition
845 temperature of which the contribution by Moynihan [58] is most relevant here. The ASTM
846 specification   for T_g by   DSC   (described   below)   is   published   at
847 www.astm.org/Standards/E1356.htm. An excellent account of the physics of the glass
848 transition as a condensed matter phenomenon is given in Angell's review article [7].
849   There are three basic definitions of a DSC "T_g" that are in common use, all of
850 which should (but not often enough) include a specification of scan rates (cooling and
851 heating). Cooling rate is more important but for glasses formed at unknown cooling rates
852 or by vapor deposition, or by other nonthermal processes, only the heating rate is known
853 but nevertheless should still be specified. The three definitions are:

854
855 (a)   *Midpoint*. The center of the transition temperature range.
856 (b)   *Onset*. The temperature at which departure from the glassy heat capacity first
857 occurs in a DSC heating scan. It is often determined by drawing a tangent line through the
858 point of inflection of $C_p(T)$ and taking T_g to be the temperature at which this line intersects
859 the extrapolated glassy heat capacity. It typically corresponds to the temperature at which
860 the excess heat capacity over that of $C_{pg}(T)$ is $5 - 10\%$ of $\Delta C_p(T_g)$.

861 (c)   *Glassy Fictive Temperature* (no annealing). Computed from integration of the heat
862 capacity. This is the best definition but also the least convenient. It typically has a similar
863 value to the onset definition if the heating and cooling rates are comparable.
864 As noted the first two definitions apply to both cooling and heating but values from
865 cooling data are preferred. One reason for preferring cooling is that heat capacity
866 overshoots and a strong dependence on the TNM nonlinearity and nonexponentiality
867 parameters x and β (see below) make the heating data more dependent on material and
868 thermal history [8].
869   As illustration of this issue consider the question "what is 'T_g' for an annealed glass
870 compared with a non-annealed glass?" The answer depends on how T_g is defined. As just
871 noted the best definition of T_g is the glassy state value of the fictive temperature T_f' and

872 this *decreases* with annealing. However upon reheating enthalpy recovery occurs at higher
873 temperatures because of nonlinearity – the lower glassy fictive temperature lengthens the
874 starting average relaxation time so that higher temperatures must be reached before the
875 average relaxation time becomes short enough for relaxation back to equilibrium to occur.
876 The heat capacity increase from glassy values to liquid values upon heating therefore
877 begins at a higher temperature and the midpoint and onset definitions of T_g *increase*.
878   The value of "T_g" that has been discussed above is generally not of great
879 importance to the detailed kinetics of structural relaxation because the temperature
880 dependencies of structural relaxation times scale with T_g and the value of T_g simply shifts
881 the transition range along the temperature axis. An exception to this is that annealing
882 behavior at temperature T_a is a strong function of $T_g–T_a$. Another exception is the
883 composition dependence of "T_g" for binary mixtures of materials with very different
884 values of T_g (polymer/solvent mixtures for example). The dependence of T_g on the
885 concentration c of the lower T_g component is often well described by
886

887 $$T_g\left(c\right) = T_g^0 \exp\left[-\left(kc\right)^\beta\right],\tag{4.75}$$

888

889 where T_g^0 is the higher value of T_g and k and β are empirical constants. Equation (4.75)
890 was discovered and used by the present author in 1989 [59] without knowledge of the
891 papers by Phillies et al., the first of which was published in 1985 [60]. The latter paper
892 also discussed power laws for molecular weight and probe radius for light scattering that
893 are subsumed into k in eq. (4.75).
894

895 4.8.3.3 Thermodynamic Aspects of the Glass Transition

896   The isobaric heat capacity of a supercooled liquid exceeds that of the crystal at
897 the same temperature so that the excess entropy of a liquid over that of the crystal
898 decreases with decreasing temperature. Extrapolations for many materials suggest that
899 this excess entropy would vanish at a temperature well above absolute zero. At this
900 temperature the entropy of the supercooled liquid equals that of the crystal and if the
901 same trend were to extend down to absolute zero the entropy of the liquid would be
902 less than that of the crystal, in conflict with the third law of thermodynamics. This
903 difficulty was first recognized by Kauzmann [61] and the extrapolated temperature at
904 which the supercooled liquid and crystal entropies become equal is known as the
905 Kauzmann temperature T_K. The extrapolation is often referred to as the Kauzmann
906 "paradox" because it seems paradoxical that the intervention of a kinetic event, the
907 observed glass transition, averts rather than resolves a thermodynamic impossibility. The
908 value of T_K is calculated by equating the excess entropy of the liquid over that of the
909 crystal to the entropy of melting ΔS_m
910

911 $$\Delta S_m = \int_{T_K}^{T_m}\left(\frac{\left[C_{pl} - C_{pg}\right](T)}{T}\right)dT,\tag{4.76}$$

912

913 where T_m is the melting temperature. The uncertainty in T_K is large mainly because $\Delta C_p(T)$
914 is obtained by extrapolation but also in part because of possible different crystal
915 forms with different values of T_m and ΔS_m. For some polymers the uncertainty is even
916 larger because of the need to correct for tacticity and partial crystallinity. As noted
917 above (§4.8.2) Goldstein [29,30] has argued that $\Delta C_p(T)$ is probably not entirely
918 configurational and may contain significant contributions from vibrational and secondary
919 relaxation sources. He estimated that between 20 and 80% of $\Delta C_p(T)$ could originate from
920 non-configurational sources and noted that this renders even more uncertain the
921 extrapolations required to assess T_K. However, as noted in the discussion of the Adam-
922 Gibbs model (§4.8.1), it is possible that all contributions to $\Delta C_p(T)$ contribute to the
923 relaxation kinetics so that how ΔC_p is partitioned is irrelevant. In any event calculated
924 values of T_K are always found to be less than T_g although in some cases the difference
925 can be as small as 20 K [62,63]. The value of T_K is often close to T_0 of the VTF equation
926 [64], suggesting again that the kinetic and thermodynamic aspects of the glass transition are
927 related.
928   Three resolutions of the thermodynamic difficulties imposed by $T_K>0$ have been
929 suggested. One is that the extrapolation of excess entropy to low temperatures has no
930 firm basis and that the prediction $T_K>0$ is a spurious result of inappropriate
931 extrapolation [65,66]. As noted already, however, the extrapolation is only 20 K or so for
932 some materials and a nonzero T_K seems almost certain in these cases. There is also the
933 possibility that the heat capacity decreases rapidly to nearly zero rather than
934 mathematical zero at a temperature where the entropy is also small but nonzero. These
935 ideas are quantified in the next paragraph about a possible Ehrenfest 2nd order
936 transition resolving the Kauzmann problem.
937   A second resolution, suggested by Kauzmann himself [61], is that the extrapolation is
938 irrelevant because the thermodynamic driving force for crystallization would always
939 intervene before the entropy problem manifested itself. However this intervention has
940 been shown to be extremely unlikely in some systems [67], and it may actually be
941 impossible in two bizarre systems (CrO_3-H_2O [68] and RbAc–H_2O [69]) for which
942 T_g exceeds the (extrapolated) eutectic temperature (the Kauzmann analysis can be
943 applied to eutectic mixtures [67]). Also, a specific thermodynamic mechanism for
944 crystallization always preventing low values of entropy to be attained has apparently not
945 yet been suggested.
946   The third resolution is that an Ehrenfest second-order transition occurs at T_K
947 at which $\Delta C_P(T)$ falls rapidly (simplistically instantaneously) to zero, similar to that
948 which is observed kinetically at T_g. The putative Ehrenfest second-order transition
949 temperature T_K is of course unobservable because of kinetic factors. It is difficult to refute
950 this hypothesis other than to dismiss it as an artifact of extrapolation, but as has just
951 been noted this objection is itself weakened by the fact that very short extrapolations are
952 needed in some cases. Furthermore an entropically based second-order transition at T_K
953 has been derived for polymers by Gibbs and DiMarzio [70], and although this
954 theory has been criticized [71] its predictions agree well with experimental observations
955 near T_g, including those on the effect of molecular weight on T_g for polymeric rings
956 [72,73]. There are also several two state models ([74,75] for example) that predict that
957 $\Delta C_p(T)$ passes through a maximum at T_{max} which is necessarily below T_g because such a

958 maximum has never been observed. If these models accommodate sharp decreases in
959 $\Delta C_p(T)$ below T_{max} then they could essentially resolve the Kauzmann "paradox" without
960 invoking an ideal Ehrenfest second order transition. For example a heat capacity function
961 that mirrors the Lorentz loss function
962

963 $$\Delta C_p(T) = \frac{C\Omega T}{1+\Omega^2 T^2},\tag{4.77}$$

964

965 where C is a constant, has a maximum at $T_{max} = 1/\Omega$ and a sharp decrease for $T < T_{max}$. Note that
966 for $T \gg T_{max}$ eq. (4.77) yields $C_p(T) \propto 1/T$ that is often approximately observed, and that as T
967 approaches T_{max} from above the T dependence becomes weaker than $1/T$, as observed for many
968 polymers [31]. Preliminary results [76] indicate that a good fit to the Fulcher equation is obtained
969 from the heat capacity function given by eq. (4.77) for the temperature range T_g to $1.5T_g$ with a
970 T_0 value of about $T_{max}/3$ [76]. Other preliminary calculations [76] suggest that good Fulcher fits
971 also obtain using a combination of two halves of such "Debye loss" functions, in which eq.
972 (4.77) describes C_p for $T > T_{max} = 1/\Omega$ and a narrower version
973

974 $$\Delta C_p(T) = \frac{C(\Omega T)^f}{1+(\Omega T)^{2f}}\ (f > 1)\tag{4.78}$$

975

976 for $T < T_{max}$. Larger values of f produce sharper low frequency decreases in $C_p(T)$ that in the
977 limit $f \to \infty$ approaches the instantaneous decrease approximation. These heat capacity functions
978 also yield good Fulcher fits with T_0 values that approach the temperature $T_{1/2} < T_{max}$ at which ΔC_p
979 is half the maximum. Preliminary analyses [76] suggest that the ratio $R = T_0/T_{1/2}$ is
980 approximately given by
981

982 $$(R-1) \approx 0.64\exp\left[-2.33(f-1)\right].\tag{4.79}$$

983

984 Angell [77] has proposed modifications to the Kauzmann analysis that suggest that a first
985 order transition, rather than an Ehrenfest second order transition, occurs at the low temperature
986 limit of a supercooled liquid. However true this may be it does not change the Adam-Gibbs
987 ansatz for relaxation times because it only affects the calculation of T_K and does not affect S_c
988 apart from its behavior deep in the glassy state, and the latter does not affect the Adam-Gibbs
989 model above T_g.
990 The entropy is not required to reach mathematical zero for the Kauzmann analysis to be
991 valid – very small values such as those that Fermi [1] referred to as not theoretically impossible
992 (see §4.2.8) would suffice. For example the degrees of freedom that contribute to the boson peak
993 (§4.2.8) are plausible sources for such small entropies.
994 The Kauzmann analysis is not the only factor that suggests a thermodynamic
995 dimension to the glass transition - two others also support it:
996 (a) Glassy state relaxation data indicate that not only the creep data shown in [41] but
997 also relaxation data for thermodynamic properties such as volume and enthalpy also shift
998 to longer time scales with annealing. As noted in [41] this implies a link between the
999 thermodynamic and nonlinear kinetic aspects of glassy state relaxation.

1000   (b)   There is compelling circumstantial evidence that, for two component mixtures that
1001   are predicted or inferred to have an upper consulate phase separation temperature below
1002 T_g, the values of T_g are almost independent of composition [78]. For example a
1003   composition invariant T_g has been observed in the LiCl-H$_2$O system in which phase
1004   separation is directly observed [69,79]. This near constancy of T_g with composition
1005   corresponds to the near constancy of the chemical potential of each component and a link
1006   between thermodynamics and kinetics seems inescapable in these cases.
1007

1008   4.8.3.4 Kinetics of the Glass Transition

1009   The mathematical description of these kinetics must necessarily incorporate those of the
1010   supercooled liquid state (§4.8.1) and the glassy state (§4.8.2) as limiting cases. We describe here
1011   only those formalisms that invoke the equilibrium temperature T and the fictive temperature T_f –
1012   others such as the KAHR description are discussed in [8]. There are two expressions for
1013 $\tau_0\left(T,T_f\right)$ in common use. The Tool-Narayanaswamy-Moynihan (TNM) expression [80] is a
1014   generalization of the Arrhenius equation:
1015

1016 $$\tau_0\left(T,T_f\right) = A_{TNM}\,\exp\left[\frac{xh}{RT} + \frac{(1-x)h}{RT_f}\right], \tag{4.80}$$

1017
1018   where $0 < x \leq 1$ is sometimes referred to as the nonlinearity parameter. The value of h can be
1019   obtained from [80]
1020

1021 $$\frac{h}{R} \approx \frac{-d\ln Q_c}{d\left(1/T_f{'}\right)}, \tag{4.81}$$

1022
1023   where Q_c is the cooling rate (not an especially good nomenclature but it is entrenched). However
1024   the uncertainties are large (typically about $\pm 20\%$).
1025   The NLAG ("Nonlinear Adam-Gibbs") or SH ("Scherer-Hodge") expression [25,26] is
1026   obtained from the AG equation (4.58) by assuming that S_c is a function of T_f rather than of T:
1027

1028 $$S_c\left(T_f\right) = C\left(1 - T_2/T_f\right), \tag{4.82}$$

1029
1030   so that
1031

1032 $$\tau_0\left(T,T_f\right) = A_{SH}\,\exp\left[\frac{B_{SH}}{T\left(1 - T_2/T_f\right)}\right]. \tag{4.83}$$

1033
1034   Equation (4.83) has several names: Adam-Gibbs-Vogel (AGV), Adam-Gibbs-Fulcher (AGF), in
1035   addition to NLAG and Scherer-Hodge (the last name is not this author's choice but is
1036   increasingly common and so is used henceforth). The full and partial temperature derivatives of
1037   eq. (4.83) are
1038

1039
$$\frac{d \ln \tau_0(T)}{d(1/T)} = \frac{B_{SH}}{(1 - T_2/T)^2} = \frac{h}{R} \qquad (4.84)$$

1040
1041   and
1042

1043
$$\left[\frac{\partial \ln \tau_0(T)}{\partial(1/T)} \right]_{T_f} = \frac{B_{SH}}{(1 - T_2/T_f)} = \frac{xh}{R}. \qquad (4.85)$$

1044
1045   Applying eqs. (4.84) and (4.85) to the glass transition temperature range where the
1046   approximation $T \approx T_f \approx T_g$ is appropriate reveals that the TNM and SH parameters are related as
1047   [8, 26]
1048
1049 $$x \approx 1 - T_2/T_g; \qquad (4.86)$$

1050
1051 $$T_2 = T_g(1 - x) \qquad (4.87)$$

1052
1053   and
1054
1055 $$B_{SH} \approx x^2 h/R \approx (1 - T_2/T_g)^2 h/R; \qquad (4.88)$$

1056
1057 $$\frac{h}{R} = \frac{B_{SH}}{(1 - T_2/T_g)^2}, \qquad (4.89)$$

1058
1059   where T_g refers to the onset definition that is closer to the glassy state. Equation (4.89) is a
1060   generalization of eq. (4.49) that applies to the nonequilibrium glass transition temperature range.
1061   Equations (4.86) - (4.89) have proven to be good approximations.
1062   A more general AG expression for the TNM nonlinearity parameter x in terms of $\Delta C_p(T_g)$
1063   and the residual configurational entropy S_{cg} [8] is
1064
1065 $$x_{AG} \approx \frac{S_{cg}}{S_{cg} + \Delta C_p(T_g)}, \qquad (4.90)$$

1066
1067   where again T_g refers to the onset definition. Equation (4.90) predicts lower values of x for larger
1068   values of $\Delta C_p(T_g)$ and smaller values of S_{cg}.
1069   The relationship between the TNM nonlinearity parameter x and the Struik shift
1070   parameter μ is not simple. Essentially the Struik relation is a special case of TNM. A simplified
1071   analysis for restricted thermal histories has been given for pharmaceutical glasses [81] in which
1072   it was noted that μ depends on the annealing temperature T_a and the WW nonexponentiality
1073   parameter β as well as the nonlinearity parameter x.
1074   The nonlinearity parameter x has been shown to be inversely related to the Angell
1075   fragility parameter m for the Scherer-Hodge equation [8,17,26]. Since the SH equation is usually

1076 a good description of $\ln \tau_0 \left(T, T_f \right)$ a generally inverse relation between x and m seems probable
1077 although a rigorous mathematical derivation is not yet at hand. However a more general analysis
1078 than SH establishes some specific conditions required for an inverse relation between x and m to
1079 hold and contains the SH result as a special case. The relation
1080

1081 $$\tau_0 \left(T, T_f \right) = A_{mx} \exp \left[f\left(T\right) g\left(T_f\right) \right] \tag{4.91}$$

1082

1083 is assumed, that apart from the separation of variables is the most general function possible. The
1084 corresponding fragility index m given by eq. (4.53) is (for $T_f = T$)
1085

1086 $$m = \left[\frac{1}{RT_g \ln\left(10\right)} \right] \left\{ f\left(T\right) \left[dg\left(T\right)/d\left(1/T\right) \right] + g\left(T\right) \left[df\left(T\right)/d\left(1/T\right) \right] \right\}. \tag{4.92}$$

1087

1088 Full and partial differentiation of eq. (4.92) with respect to $1/T$ yields
1089

1090 $$\frac{h}{R} = \frac{d \ln \tau_0 \left(T_f = T, T \right)}{d\left(1/T\right)} = g\left(T\right) \frac{df}{d\left(1/T\right)} + f\left(T\right) \left. \frac{dg}{d\left(1/T\right)} \right|_{T=T_g} \tag{4.93}$$

1091
1092 and
1093

1094 $$\frac{xh}{R} = \left. \frac{\partial \ln \tau_0 \left(T_f, T \right)}{\partial\left(1/T\right)} \right|_{T=T_f=T_g} = g\left(T_g\right) \left. \frac{df}{d\left(1/T\right)} \right|_{T=T_g}, \tag{4.94}$$

1095
1096 so that
1097

1098 $$\frac{1}{x} = \left. \frac{g \dfrac{df}{d\left(1/T\right)} + f \dfrac{dg}{d\left(1/T\right)}}{g \dfrac{df}{d\left(1/T\right)}} \right|_{T=T_f=T_g} = \left. \left[1 + \frac{d \ln g / d\left(1/T\right)}{d \ln f / d\left(1/T\right)} \right] \right|_{T=T_f+T_g}. \tag{4.95}$$

1099
1100 Equations (4.92) and (4.95) yield
1101

1102 $$x^{-1} = \left. \frac{mRT_g \ln\left(10\right)}{g df / d\left(1/T\right)} \right|_{T=T_f=T_g}. \tag{4.96}$$

1103

1104 The function $\left. df / d\left(1/T\right) \right|_{T_g}$ must be approximately equal to xh/R to ensure consistency with the
1105 experiment so that
1106

1107
$$\frac{mR^2 T_g \ln(10)}{hg(T_g)} \approx 1.$$
(4.97)

1108

1109 The relationship between x and m therefore depends on the x-dependence of $g(T_g)$. For the SH
1110 expression $g(T_g) = (1 - T_2/T_g)^{-1} \approx x^{-1}$ and m is exactly inversely proportional to x.

1111
1112 4.3.3.5 Thermorheological Complexity *(TRC)*

1113   All the analyses discussed so far consider the TNM and SH parameters to be independent
1114 of temperature. However there are several reports throughout the literature that some of these
1115 parameters are temperature dependent, in particular that the distributions of relaxation times
1116 depend on both T and T_f. The following discussion of this possibility draws heavily from [82].
1117   Consider first an Arrhenius temperature dependence for the structural relaxation time τ_i
1118 corresponding to the component E_i of a distribution of activation energies
1119

1120
$$\ln \tau_i = \ln A_A + \frac{E_i}{RT}.$$
(4.98)

1121

1122 For a Gaussian distribution of activation energies with standard deviation σ_E the standard
1123 deviation $\sigma_{\ln\tau}$ in the corresponding logarithmic Gaussian distribution of relaxation times $g(\ln\tau)$
1124 is therefore

1125

1126
$$\sigma_{\ln\tau} = \frac{\sigma_E}{RT}.$$
(4.99)

1127

1128 Thus any distribution of relaxation times is temperature dependent if there is an underlying
1129 distribution of activation energies. Any physically reasonable distribution of activation energies
1130 for condensed media is unlikely to be a delta function so that thermorheological simplicity must
1131 generally be an approximation. For nonlinear expressions of relaxation times the distribution of
1132 $\ln(\tau)$ is a function of T_f as well as T. For example the SH expression [eq. (4.104) below] yields,
1133 for a Gaussian distribution in B,

1134

1135
$$\sigma_{\ln\tau} = \frac{\sigma_B}{T(1 - T_2/T_f)}.$$
(4.100)

1136

1137 Gaussian standard deviations have their counterparts in the widths of other distributions such as
1138 WW so that eqs. (4.99) and (4.100) are generally applicable.
1139   Implementation of TRC phenomenologies requires that the decay function be expressed
1140 as a Prony series with coefficients g_i that are T and T_f dependent [82]. For the WW decay
1141 function for example
1142

1143 $$\exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right] = \sum_{i=1}^{N} g_i\left(T, T_f\right) \exp\left[-\left(\frac{t}{\tau_i}\right)\right],$$ (4.101)

1144
1145 where the best fit values of both N and g_i depend on β. This is computationally expensive
1146 because the coefficients g_i must be recalculated at every temperature step (although doing so
1147 every $n > 1$ steps may be a good approximation). Estimates by the present author suggest that
1148 computation times are around $10^{0\pm1}$ days, depending on $\beta\left(T_g\right)$.

1149

1150 4.9   Experimental DSC Results
1151   The DSC technique ("<u>D</u>ifferential <u>S</u>canning <u>C</u>alorimetry") is not strictly calorimetry but
1152 the name is embedded in the literature and changing it here would serve no useful purpose. The
1153 technique measures heat capacity by recording the heat flow into a sample needed to maintain a
1154 programmed temperature during cooling and reheating. It is described here because enthalpy
1155 relaxation is a good surrogate for structural relaxation in general, and there are abundant
1156 experimental DSC data available for analysis because the technique is so experimentally
1157 convenient. Modifications of the technique such as modulated DSC (MDSC) are not discussed.
1158   The term "differential" originates from the fact that the difference in heat inputs to two
1159 instrument pans (sample and reference) is measured in order that the sample and reference be at
1160 the same temperature during heating and cooling. Heat input into the reference pan is adjusted to
1161 maintain the specified rate of change of temperature – for cooling this requires a cold bath
1162 (typically ice/water, dry ice or liquid nitrogen) in thermal contact with the reference pan (for
1163 liquid nitrogen coolant helium is needed as a carrier gas because nitrogen could obviously
1164 condense). The heat capacity is computed from

1165

1166 $$C_p\left(T\right) = \left(\frac{dq}{dt}\right) \bigg/ \left(\frac{dT}{dt}\right) = \left(\frac{dq}{dt}\right) \bigg/ Q_{c,h},$$ (4.102)

1167

1168 where $Q_{c,h}$ is the cooling/heating rate and dq/dt is the measured differential heat input (typically
1169 given in mW). Note that for any given C_p the differential heat input dq/dt is proportional to $Q_{c,h}$
1170 so that there is a lower limit to $Q_{c,h}$ that is determined by instrumental sensitivity.

1171   Thermal lag shifts the DSC temperature calibration by an amount $\tau_{th}\dot{T}_h$ ([83] and
1172 references therein). This is the basis of temperature calibration that usually uses the melting
1173 temperature of a standard material (often indium) and preferably of two (the second is often
1174 zinc). However the value of τ_{th} for pure metals is smaller than for most amorphous materials,
1175 especially polymers, because of the larger thermal conductivity of metals. Hodge and Heslin [83]
1176 reported a value of 5 ± 0.5 s obtained from indium temperature calibration compared with 15-17
1177 s for their polymer sample. This discrepancy is atypically large because the sample shape was
1178 deliberately irregular in order to maximize heat transfer effects, but it does illustrate the
1179 uncertainties in temperature calibration.
1180   Sample preparation is straight forward and experimental reproducibility is generally
1181 excellent for inorganic and simple organic glasses. Polymers present several complications of
1182 which sample reproducibility is the most important. Variables such as molecular weight,
1183 molecular weight distribution and degree of crystallinity are too often not reported or are just

1184   implicit in the identification of the manufacturer and/or product name. Crystallinity and crystal
1185   morphology can also be affected by thermal histories before a DSC run – for example the
1186   temperature and time spent above T_g for stabilization. Even when these are stated it is difficult to
1187   quantify any material changes, particularly in crystallinity or crystal morphology. For example
1188   changes in the micro crystallinity of PVC with the temperature excursions required to make the
1189   traditional sample disk that were employed by Pappin et al. [84] were almost certainly the cause
1190   of their TNM parameters being significantly different [8] from those found by Hodge and Berens
1191   [85], who used the original powdered PVC material that was sent to the authors of [85].
1192   The reproducibility of the heat capacity over the glass transition temperature range during
1193   constant cooling and heating rates is a good test of the TNM formalism and it passes with flying
1194   colors. Hodge and Berens [50] later introduced annealing times into the Moynihan calculations.
1195   All these calculations combine the TNM expression eq. (4.80) or SH expression eq. (4.83), the
1196   reduced time eq. (4.68), and Boltzmann superposition (Chapter One). These calculations are
1197   discussed here because they illustrate many aspects of structural relaxation kinetics and provide
1198   many insights into the glass transition phenomenon.
1199   During DSC scanning both T and T_f change with time (for isothermal annealing only T_f
1200   changes of course). Thus the reduced time eq. (4.68) can be expressed in terms of the TNM eq.
1201   (4.80) or SH eq. (4.83) using time dependent T and T_f:
1202

1203
$$\tau_0(t) = A_{TNM} \exp\left[\frac{xh}{RT(t)} + \frac{(1-x)}{RT_f(t)}\right] \qquad (4.103)$$

1204
1205   or
1206

1207
$$\tau_0(t) = A_{SH} \exp\left[\frac{B_{SH}}{T(t)\left[1 - T_2/T_f(t)\right]}\right]. \qquad (4.104)$$

1208
1209   This is the first step in computing $T_f[T(t)]$ and thence dT_f/dT. The second step is to introduce
1210   Boltzmann superposition by representing rate cooling and heating as a sequence of temperature
1211   jumps ΔT (typically constant but not necessarily so, see below). The final result for TNM is
1212

1213
$$T_f(t) = T_0 + \int_{T_0}^{T}\left(1 - \exp\left\{-\left[\int_0^t \frac{dt'}{A_{TNM}\exp\left\{\frac{xh}{RT'(t')} + \frac{(1-x)h}{RT_f(t')}\right\}}\right]^{\beta}\right\}\right) dT' \qquad (4.105)$$

1214
1215   and that for SH is
1216

1217
$$T_f(t) = T_0 + \int_{T_0}^{T} \left(1 - \exp\left\{ -\left[\int_0^t \frac{dt'}{A_{SH} \exp\left\{ \frac{B_{SH}}{T'(t')\left[1 - T_2 / T_f(t') \right]} \right\}} \right]^\beta \right\} \right) dT'.$$
(4.106)

1218
1219 For eqs. (4.105) and (4.106) the integral within the square brackets is the reduced time integral
1220 eq. (4.68) and the occurrence of T_f on both sides of the equations reflects nonlinearity. For
1221 computations the integrals are of course replaced by summations for which dT' is replaced by
1222 $\Delta T'$ and dt' is replaced by $\Delta t'$. The value of $\Delta t'$ is variable for annealing, and $\Delta T'$ is variable for
1223 large overshoots in C_p^N [83], as discussed below.

1224   The agreement between computed TNM and experimental C_p^N is generally excellent for
1225 inorganic materials and thermal histories without annealing [8]. The SH formalism does not
1226 generally improve on these results. For organic polymers and for thermal histories that include
1227 isothermal annealing [86], however, the agreement is less satisfactory. The reasons for these
1228 discrepancies are discussed below and include the fact that the gamut of TNM parameters for
1229 organic polymers is typically larger, in particular the lowest values of x and β for polymers are
1230 much smaller than those of the lowest values for inorganic materials [8].

1231
1232 4.9.1   Data Analysis
1233   The general computation conditions reported by Hodge and Heslin [83] are listed below.
1234 Unfortunately these conditions cannot be compared with those given in most other reports
1235 because the latter often provide insufficient detail. Computation times for thermal histories
1236 without annealing are typically about 2 s on modest computers using Matlab® or Gnu Octave,
1237 and optimization times for thermal histories that include annealing are typically 20 – 30 minutes.
1238 (a) The currently used value of ΔT is 0.1 K except for C_p^N overshoots in excess of 1.0. For the
1239 latter the temperature steps are reduced in inverse proportion to C_p^N for the previous step – for
1240 example for $C_p^N = 2.5$ the following temperature step is $0.1/2.5 = 0.04$ K. Computed values of
1241 dT_f/dT at the regular temperature intervals needed for comparison with experiment are obtained
1242 by cubic spline interpolation.
1243 (b) Annealing times are divided into 100 logarithmically even intervals per decade, from 0.1s to
1244 the annealing time t_a in seconds, using the Matlab®/GNU Octave *logspace* function. For
1245 example for $t_a = 24$ hours $= 8.64 \times 10^4$ s the number of annealing intervals is 594. Very long
1246 annealing times increase the calculation time beyond the 2 s or so needed for thermal histories
1247 without annealing.
1248 (c) The WW function is used explicitly (rather than being approximated as a Prony series as
1249 done earlier to reduce computation times that are no longer problematic).
1250 (d)   The Matlab®/GNU Octave *fminsearch* (simplex) function is used for optimization. This
1251 algorithm allows optimization of all four TNM and SH parameters and does not readily get
1252 trapped in a local minimum.

1253   Thermal lag effects are corrected for by using experimentally determined thermal
1254   constants τ_{th}. The effects of τ_{th} have been discussed ever since the DSC technique was
1255   introduced (see refs in [8]) and have been analyzed in detail by Hodge and Heslin [83] with
1256   regard to the TNM formalism. The Hodge/Heslin value of τ_{th} was determined from the changes
1257   in heat flow and measured heating rate as a function of time following a programmed change in
1258   heating rate and equating τ_{th} to the displacement of one from the other (roughly 15 s in this
1259   case). The curve shapes were about the same so that this displacement implied a approximately
1260   exponential Heaviside response function with a time constant of 15 s. When data were corrected
1261   for this time constant the experimental C_p^N data for no annealing were independent of the ratio
1262 Q_h/Q_c within uncertainties, as predicted by the TNM model (including a Q_h/Q_c = 25 K/min
1263   history for which the original data exhibited no overshoot at all). Since the TNM model gives a
1264   very good account of C_p^N when $Q_h = Q_c$ the confirmation of this prediction using an exponential
1265   Heaviside response function indicates that the latter is a good approximation.
1266   The expression for deconvoluting observed experimental data $C_{p,obs}^N$ to produce the true
1267   "original" $C_{p,orig}^N$ is
1268

$$1269 \quad C_{p,orig}\left(t\right) = C_{p,obs}\left(t\right) + \tau_{th}\left(\frac{dC_{p,obs}\left(t\right)}{dt}\right) \tag{4.107}$$

1270
1271   or
1272

$$1273 \quad C_{p,orig}\left(T\right) = C_{p,obs}\left(T\right) + \tau_{th}Q_h\left[\frac{dC_{p,obs}\left(T\right)}{dT}\right]. \tag{4.108}$$

1274
1275   A similar analysis is implied in publications by Hutchinson et al. [87,88] although no details
1276   were given.

1277   ### 4.9.2 Sub-T_g Annealing Endotherms
1278   As noted above Hodge and Berens [85] were the first to apply the TNM formalism to
1279   polymers and thermal histories that included annealing. When they applied it to the polymer
1280   PVC they found that it required TNM parameters x and β far smaller than any of those reported
1281   for inorganic materials. These extreme parameters produced a surprising result – upon reheating
1282   the enthalpy lost during annealing was sometimes recovered well below the glass transition
1283   temperature range to produce sub-T_g peaks in the heat capacity. These peaks are well reproduced
1284   by the TNM and SH formalisms. Similar annealing peaks have also been observed for PMMA
1285   [86] (albeit closer to T_g) and are also well reproduced by the TNM and SN formalisms [86].
1286   The explanation of these peaks was not recognized in 1995 when the effects of annealing
1287   on polymers were reviewed [41]. To explain the peaks it is first useful to express nonexponential
1288   decay functions such as WW as a Prony series [§1.4.3.1] of exponential decay functions, with
1289   different relaxation times and weighting factors that are the equivalent of a distribution of
1290   relaxation times:
1291

1292
$$\exp\left[-\left(\frac{t}{\tau_0}\right)^\beta\right] = \sum_{n=1}^{N} g_n \exp\left(\frac{-t}{\tau_n}\right).$$
(4.109)

1293
1294   Lesikar and Moynihan [89,90] introduced a formal order parameter description of the glass
1295   transition that associated each τ_n with a fictive temperature $T_{f,n}$ such that
1296

1297
$$T_f = \sum_{n=1}^{N} g_n T_{f,n}$$
(4.110)

1298

1299   where

1300

1301
$$\sum_{n=1}^{N} g_n = 1.$$
(4.111)

1302

1303   When each τ_n was made a function of $T_{f,n}$ they found that the fits to experimental data were
1304   worse than if τ_0 (and hence all τ_n) were determined by the global T_f. This is the key to why sub-
1305 T_g endotherms can occur. During initial heating of an annealed glass with low T_f and long τ_0 the
1306   shortest τ_n components relax first and contribute to a decrease in $\langle\tau\rangle$ so that the global T_f
1307   increases towards the un-annealed value and $C_p^N \approx dT_f / dT$ also increases. Equivalently the
1308   initially rapid decrease in $\phi(t)$ for a nonexponential decay function such as WW also enables
1309   partial relaxation to occur and therefore changes the global τ_0 and T_f. The decrease in the global
1310 τ_0 makes further changes in C_p^N more rapid well below T_g. As T_f approaches the glassy T_f' that
1311   existed before annealing its rate of approach towards T_f' decreases and C_p^N decreases until the
1312   onset of the glass transition temperature range is approached at T_f ', thus producing the observed
1313   sub-T_g peak in C_p^N. This analysis also explains why sub-T_g endotherms that occur well below the
1314 T_g range are essentially superimposed on the glass transition for unannealed glasses. Note that
1315   both nonexponentiality and nonlinearity come into play here. The more rapidly the initial
1316   decrease in T_f is during heating the faster the distribution moves to shorter times because of
1317   nonlinearity, and the rapidity of the initial decrease in T_f depends on nonexponentiality.
1318   Not all sub-T_g endotherms are generated by enthalpy relaxation. There is always the
1319   possibility that they are produced by the melting of crystals or crystallites formed during
1320   annealing. A yet to be published result by Hodge [91] provides a good example of how easily the
1321   two possibilities can be confused, especially if estimates of experimental uncertainties are too
1322   pessimistic. Hodge re-analyzed the DSC data of Sartor et al. [92] on annealed hydrated proteins
1323   that exhibited broad and weak endotherms when scanned after annealing at several temperatures.
1324   The experimental uncertainties in the widths and peak heights of the endotherms were estimated

1325 to be large because of a sloping and curved background, but TNM parameters were nevertheless
1326 found that fitted the data much better than the published set of parameters; these values are [92]:
1327 $\{\ln A(s) = -80; h/R = 2.0 \times 10^4 \text{ K}; x = 1.0; \beta = 0.04\}$. The largest discrepancy between observed
1328 and calculated endotherm properties was the annealing temperature dependence of the
1329 endotherm magnitudes but this was thought to be within experimental uncertainty. However,
1330 Tombari and Johari later reported [93] that the endotherms were almost certainly due to melting
1331 of crystals of $NaCl.2H_2O$ in the commercial samples of the hydrated proteins, formed during
1332 annealing. Hodge's estimates of the experimental endotherm areas passed through a maximum at
1333 an annealing temperature 238K that was 14K below the melting temperature 252K of the
1334 crystals, at which a maximum rate of crystallization might reasonably be expected.
1335
1336 ### 4.9.3   TNM Parameters
1337   There are rough correlations between the TNM parameters x and h and between x and β
1338 [32,33,86] but they are weak and are suggestive of, rather than evidence for, any possible
1339 underlying cause. The WW β parameter has the least uncertainty and the value of h can be
1340 obtained without TNM optimization so that in principle any correlation between h and β will
1341 have the smallest statistical uncertainty, but remarkably no plot of h versus β has been published
1342 to this author's knowledge. For most of the data in Table 1 in [8] (the omitted data are those for
1343 which β is not listed) such a plot indeed reveals less scatter but the correlation remains weak, as
1344 indicated by the correlation coefficient 0.64 for h versus β compared with 0.42 for h versus x and
1345 0.41 for x versus β.
1346
1347 ### 4.9.4   SH Parameters
1348   Equations (4.87) and (4.88) have been confirmed for those cases when the TNM and SH
1349 models have been fitted to the same data. Many reported SH parameters are obtained from TNM
1350 fits using these equations because TNM parameters are much more common (many pre-date the
1351 introduction of the SH formalism). As noted above the SH formalism does not generally give
1352 improved fits compared with TNM [26] but the SH parameters can be more plausibly linked to
1353 possible molecular factors, discussed next.
1354   Consider first the AG parameters s_c^* and $\Delta\mu$ in eq. (4.62). This equation indicates that C
1355 and s_c^* are both needed before $\Delta\mu$ can be obtained from experimental values of B_{SH}. For this
1356 purpose it is convenient to assume that $\Delta C_p(T)$ is given by
1357
1358 $$\Delta C_p(T) = C'T_g/T \tag{4.112}$$
1359
1360 so that C' equals $\Delta C_p(T_g)$ and eq. (4.62) becomes
1361
1362 $$B_{SH} = \frac{N_A s_c^* \Delta\mu}{k_B C' T_g} = \frac{N_A s_c^* \Delta\mu}{k_B T_g \Delta C_p(T_g)} = \frac{N_A \ln(\Omega)\Delta\mu}{T_g \Delta C_p(T_g)} \ . \tag{4.113}$$

1363
1364 The unit of mass also needs to be defined and for this the concept of a "bead" introduced by
1365 Wunderlich and Jones [94] is helpful. Wunderlich defined the bead as the monomer segment of a
1366 polymer (such as $-CH_2-$ in polyethylene), and for small molecules it is a similarly small

1367 chemical entity (for example toluene is regarded as having two beads corresponding to the
1368 phenyl ring and the methyl substituent). For inorganic materials the bead is considered to be a
1369 rotatable unit such as a sulfate or nitrate, either as ions or groups covalently bound to a larger
1370 molecule. These examples indicate that the bead is an intuitive rather than a rigorous metric for
1371 mass.
1372   The value of s_c^* is also intuitive and is fraught with uncertainties. The most commonly
1373 assumed value is
1374
1375
$$s_c^* = k_B \ln 2 \tag{4.114}$$
1376
1377 because there is a minimum of two configurations – those before and after rearrangement. At
1378 least two exceptions to this have been discussed, however. First, Sales [95] reported on some
1379 phosphate glasses and reversed the logic by equating $\Delta\mu$ with the P – O bond strength and
1380 discussed the derived values of s_c^* in terms of the coordination number of phosphates around the
1381 Pb and Fe cations. He found that the differences in s_c^* values were consistent with the crystal-
1382 field stabilized coordination around the Fe cation being more robust than the coordination around
1383 the Pb cations: as the iron content increased from 0% to 25%Fe/75%Pb the values of s_c^*
1384 increased from 4.6 to 24.5. Thus values of s_c^* greater than $k_B \ln 2$ have some support. Second,
1385 Hodge [26] suggested that eq. (4.114) is inappropriate for polymers because of constraints
1386 imposed by consecutive covalent bonds, and eq. (4.114) was replaced by [96]
1387
1388
$$s_c^* = k_B \ln 2^3 = k_B \ln 8, \tag{4.115}$$
1389
1390 because "…two rotational states are available to each segment and [a] crankshaft motion is
1391 assumed to involve 3 segments…". If three distinguishable rotational states per segment and no
1392 crankshaft motion is assumed then for two adjacent segments
1393
1394
$$s_c^* = k_B \ln 3^2 = k_B \ln 9. \tag{4.116}$$
1395
1396 The difference between ln 8 and ln 9 is smaller than any reasonable uncertainty in s_c^*. For large
1397 nonpolymeric molecules that are not linear the crankshaft motion is irrelevant and it is
1398 reasonable to extend eq. (4.116) to
1399
1400
$$s_c^* = k_B \ln 3^{N-1}, \tag{4.117}$$
1401
1402 where N is the number of beads (segments) and N-1 is the number of rotatable bonds between
1403 them. Equation (4.117) has not been suggested before and like eq. (4.115) for polymers it has
1404 dubious statistical rigor so that values of $\Delta\mu$ derived from it must be regarded as approximate.
1405 Because of intra- and inter- molecular geometrical constraints the number of configurations for
1406 large molecules is probably less than that given by eq. (4.117) and derived values of $\Delta\mu$ should
1407 therefore be regarded as minimum ones.
1408   Hodge and O'Reilly [96] analyzed the SH parameters for five nonpolymeric organic
1409 molecules: the ortho-, meta- and para- (o-, m-, p-) isomers of indane, o-terphenyl (OTP), and tri-

1410 α-naphthyl benzene (TNB). The chemical formulae for these materials are given in [96]. Their
1411 data are discussed in detail here (more than in the original publication) for two reasons: (i) re-
1412 evaluations of s_c^* using eq. (4.117); (ii) revised SH values of $\Delta\mu$ based on these new values of s_c^*.
1413 Data from [96] are summarized in Table 4.1 that combines entries in Tables 1 and 4 of [96] as
1414 well as results from the new calculations. The values of N correspond to the original number 11
1415 as well as the number of Wunderlich segments for the three indane isomers cited in [96]. The
1416 units of $\Delta\mu$ are kJ mol^{-1}, not kJ (mol-bonds)$^{-1}$ as stated in [96]. The boldface $\Delta\mu$ entries
1417 correspond to the best estimates of N for each material.
1418
1419

TABLE 4.1

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

1420
1421   Inter-segmental rotational energy barriers ΔE are given by the values of $\Delta\mu$ divided by
1422 N-1. Using $N = 11$ for the (o-, m-, p-) indanes yields $\Delta E = 9, 6, 17$ kJ/bond, smaller than typical
1423 rotational energy barriers for isolated molecules by a factor of 2 or so and probably by more for
1424 molecules constrained in condensed media, but as noted above the cited $\Delta\mu$ values are minimum
1425 ones. The Wunderlich N values for the o-, m- and p- indane isomers are 14, 17 and 16
1426 respectively and these give even smaller values of ΔE. For OTP the number of Wunderlich
1427 segments is $113/11.3 = 10$ and the average rotational energy barrier is $61kJ/10 = 6.1$ kJ, and for
1428 TNB the number of beads $150/11.3(?) = 13$ and the average rotational energy barrier is $38kJ/13 =$
1429 3 kJ. Both these barrier energies are also too small but are again minimum ones.
1430   The weak correlations between the TNM parameters noted above in §4.9.3 become
1431 stronger when they are expressed in terms of SH parameters. In particular when the SH
1432 parameter $T_g / T_2 \approx (1-x)^{-1}$ is plotted against $B_{SH} \approx x^2 h / R$ and materials are separated into
1433 plausible different molecular types [32,33] three linear correlations are clearly evident (if two
1434 suspiciously outlying polystyrene data are removed the polymer correlation improves. There is
1435 an indisputable extrapolation towards $T_g/T_2 \to 1$ as $B_{SH} \to 0$ for each of the three correlation
1436 lines. Since B_{SH} is proportional to $\Delta\mu$ in the AG model and the proportionality constant cannot be
1437 zero the extrapolation $B \to 0$ corresponds unambiguously to $\Delta\mu \to 0$ and suggests that as $\Delta\mu$
1438 approaches zero there is no (average) barrier to prevent T_g approaching some fundamental
1439 amorphous state temperature that could be approximated by T_2 and/or T_K ("ideal glass", see
1440 §4.2.2.6). This in turn again suggests that some fundamental lower limit to T_g is possible that
1441 could have thermodynamic roots and could even be a candidate for Fermi's "not theoretically
1442 impossible" state of small but nonzero entropy at 0 K (§4.2.2.6 and [1]).
1443

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