

Part One

# Glass Transitions in Amorphous Polymers

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# Chapter 1

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## Glass Transitions in Amorphous Polymers: Basic Concepts

A window shatters, into a cloud of uncertainty.

—Michael Berardi

**G**lass transitions in amorphous materials are described primarily from a thermodynamic viewpoint, but the kinetic nature of  $T_g$  is mentioned also. The pressure dependence of first- and second-order phase transitions is compared via the Clapeyron and Ehrenfest equations, respectively. Compositional dependence of  $T_g$  in single-phase mixtures is addressed from volume and entropy continuity. The connection between fractional free volume and  $T_g$  is introduced. Then, physical variables that affect  $T_g$  are discussed in terms of their influence on free volume. Effects of molecular weight, particle size, film thickness, and surface free energy on the glass transition are also considered.

### 1.1 PHASE TRANSITIONS IN AMORPHOUS MATERIALS

Unlike crystalline solids with long-range order, glasses transform to highly viscous liquids upon heating. Amorphous materials exhibit some short-range order, but essentially no long-range order. Whereas melting is reserved for materials that exhibit some crystal structure, glass–liquid phase transitions are characterized by the continuous behavior of several thermodynamic state functions, including enthalpy, entropy, and volume. From a rigorous viewpoint, glasses do not melt, and their flow behavior is evident during the time scale of centuries in the vertical colored glass windows of medieval churches. Plasticizing additives shift the glass transition to lower temperature and increase the utility of relatively inexpensive brittle polymers.

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*Physical Properties of Macromolecules.* By Laurence A. Belfiore  
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## 1.2 VOLUME-TEMPERATURE AND ENTHALPY-TEMPERATURE RELATIONS IN THE VICINITY OF FIRST-ORDER AND SECOND-ORDER PHASE TRANSITIONS: DISCONTINUOUS THERMOPHYSICAL PROPERTIES AT $T_m$ AND $T_g$

The glass transition temperature (i.e.,  $T_g$ ) is one of the most important thermophysical properties of a polymeric material. In the glassy state below  $T_g$ , materials are usually brittle with an elastic modulus on the order of  $10^{10}$  dynes/cm<sup>2</sup> and a fracture strain of 5% or 10%. Molecular vibrations and micro-Brownian motions that produce local conformational rearrangements of the chain backbone are characteristic of glasses. In the highly viscous liquid state above  $T_g$ , materials are rubbery with an elastic modulus of  $\sim 10^7$  dynes/cm<sup>2</sup> that exhibits strong dependence on molecular weight. If chain entanglements are operative, then fracture strains easily exceed 100%. Viscous liquids exhibit molecular vibrations, conformational rearrangements of the chain backbone, and translational motion of the chain along its contour, which is called reptation. Knowledge of  $T_g$  allows one to develop a reasonably accurate picture of a material's elastic modulus over a wide temperature range. Semicrystalline polymers exhibit a melting transition. However, all materials, regardless of their molecular weight, exhibit a glass transition. It might be necessary to quench a low-molecular-weight material very rapidly from the molten state so that  $T_g$  can be observed without complications due to crystallinity. The primary objectives of this chapter are to (i) observe and measure  $T_g$  in amorphous polymers and (ii) recognize several factors that affect  $T_g$ .

It is instructive to compare the temperature dependence of intensive thermodynamic properties, like specific volume  $v$  (i.e.,  $1/\rho$ , where  $\rho$  represents density) or specific enthalpy  $h$ , in the vicinity of  $T_g$  and  $T_m$ . For a low-molecular-weight solid that is essentially 100% crystalline, the temperature dependence of its density or specific enthalpy exhibits an abrupt discontinuity at the melting temperature (i.e.,  $T_m$ ). Some of the discontinuous intensive thermodynamic properties at  $T_m$  are  $\Delta(1/\rho_{\text{melt}})$ ,  $\Delta v_{\text{melt}}$ ,  $\Delta h_{\text{melt}}$ , and  $\Delta s_{\text{melt}}$ , where  $s$  is specific entropy and  $\Delta$  signifies the difference between a thermodynamic property slightly above and slightly below the transition temperature. These discontinuous observables exhibit a step increase at  $T_m$  for all materials, except H<sub>2</sub>O in which  $\Delta(1/\rho_{\text{melt}})$  and  $\Delta v_{\text{melt}}$  are negative. Melting is classified as a first-order phase transition because all first and higher derivatives of the chemical potential are discontinuous at  $T_m$ . This is illustrated as follows via the extensive Gibbs free energy of a pure material,  $G(T, p, N)$ , in terms of its natural variables: temperature  $T$ , pressure  $p$ , and total moles  $N$ , which represent complete thermodynamic information about the system. According to the phase rule, three degrees of freedom (i.e.,  $T$ ,  $p$ , and  $N$ ) must be specified for a unique description of *extensive* thermodynamic properties when a pure material exists as a single phase. The phase rule stipulates that there are two degrees of freedom for single-phase behavior of a pure material, but extensive properties require one additional degree of freedom associated with total system mass. The total differential of the Gibbs potential is

$$dG = \left\{ \frac{\partial G}{\partial T} \right\}_{p,N} dT + \left\{ \frac{\partial G}{\partial p} \right\}_{T,N} dp + \left\{ \frac{\partial G}{\partial N} \right\}_{T,p} dN$$

The temperature, pressure, and mole number coefficients of  $G$  are defined as follows:

$$\left\{ \frac{\partial G}{\partial T} \right\}_{p,N} = -S; \quad \left\{ \frac{\partial G}{\partial p} \right\}_{T,N} = V; \quad \left\{ \frac{\partial G}{\partial N} \right\}_{T,p} = \mu$$

where  $S$  is extensive entropy,  $V$  is extensive volume, and  $\mu$  is the chemical potential. Since total moles  $N$  represents the only extensive independent variable for  $G$ , as described above, Euler's integral theorem for homogeneous functions of the first degree with respect to system mass yields the following result:

$$G = N \left\{ \frac{\partial G}{\partial N} \right\}_{T,p} = N\mu$$

Hence, the total differential of  $G$ , based on Euler's integration, is

$$dG = N d\mu + \mu dN$$

and this should be compared with the previous result for the total differential of  $G$ :

$$dG = -S dT + V dp + \mu dN$$

One arrives at the Gibbs–Duhem equation via this comparison, which reveals that an *intensive* quantity, like the chemical potential of a pure material, requires specification of two independent variables (i.e.,  $T$  and  $p$ ) for a unique description of single-phase behavior:

$$d\mu = - \left\{ \frac{S}{N} \right\} dT + \left\{ \frac{V}{N} \right\} dp = -s dT + v dp$$

From the previous equation, the first derivatives of chemical potential with respect to either temperature or pressure are

$$\left\{ \frac{\partial \mu}{\partial T} \right\}_p = -s; \quad \left\{ \frac{\partial \mu}{\partial p} \right\}_T = v$$

If the system contains several components, then the temperature and pressure coefficients of the chemical potential of species  $i$  are written in terms of partial molar entropy and partial molar volume of component  $i$ , respectively. Since molar entropy and molar volume of pure materials and mixtures are discontinuous at  $T_m$ , and these intensive properties are obtained from the first derivatives of  $\mu$ , melting is classified as a first-order thermodynamic phase transition. If all first derivatives of  $\mu$  are discontinuous at  $T_m$ , then all higher-order derivatives of  $\mu$  are also discontinuous upon melting. An  $n$ th-order phase transition is defined as one in which the  $n$ th derivatives of  $\mu$  (including mixed  $n$ th partial derivatives) are the first ones that yield discontinuous thermodynamic properties at the phase transition temperature. By definition, the zeroth-order derivatives of  $\mu$  are continuous at  $T_m$ , and the following statements represent the criterion of chemical equilibrium for pure materials, based on the integral

and differential methods, respectively:

$$\begin{aligned}\mu_{\text{Solid}}(T_m^-) &= \mu_{\text{Liquid}}(T_m^+) \\ d\mu_{\text{Solid}}(T_m^-) &= d\mu_{\text{Liquid}}(T_m^+)\end{aligned}$$

Now, consider the temperature dependence of specific volume and specific enthalpy in the vicinity of  $T_g$ . These thermodynamic properties are continuous at  $T_g$ , but their slopes change at the phase transition in the following manner:

$$\begin{aligned}\left\{ \frac{\partial v}{\partial T} \right\}_{p;\text{Liquid}} &> \left\{ \frac{\partial v}{\partial T} \right\}_{p;\text{Glass}} \\ \left\{ \frac{\partial h}{\partial T} \right\}_{p;\text{Liquid}} &> \left\{ \frac{\partial h}{\partial T} \right\}_{p;\text{Glass}}\end{aligned}$$

The first inequality suggests that thermal expansion coefficients  $\alpha$  increase abruptly upon heating at  $T_g$ , because

$$\begin{aligned}\alpha &= \left\{ \frac{\partial \ln v}{\partial T} \right\}_p = \frac{1}{v} \left\{ \frac{\partial v}{\partial T} \right\}_p \\ \{v\alpha\}_{\text{Liquid}} &> \{v\alpha\}_{\text{Glass}}\end{aligned}$$

Since specific volume is continuous at  $T_g$ , the previous inequality reveals that

$$\begin{aligned}\alpha_{\text{Liquid}} &> \alpha_{\text{Glass}} \\ \Delta\alpha &= \alpha_{\text{Liquid}} - \alpha_{\text{Glass}} > 0\end{aligned}$$

where, in this case,  $\Delta$  represents the difference between thermodynamic properties slightly above  $T_g$  (i.e., highly viscous liquid) and slightly below  $T_g$  (i.e., rigid glass). Since the temperature dependence of specific enthalpy increases above  $T_g$ , and

$$C_p = \left\{ \frac{\partial h}{\partial T} \right\}_p = T \left\{ \frac{\partial s}{\partial T} \right\}_p$$

it follows directly that specific heats are larger for liquids than they are for the corresponding glasses. Hence  $\Delta C_p > 0$ .

There are no known exceptions to the previous two inequalities, which indicate that coefficients of thermal expansion and specific heats experience step increments at  $T_g$  when materials are heated from the glassy state into the highly viscous liquid state. By definition,  $T_g$  is a second-order thermodynamic phase transition because volume, enthalpy, and entropy are continuous but the temperature derivatives of these thermophysical properties are discontinuous. If  $\mu = \mu(T, p)$  for a pure material, then there are three second partial derivatives of the chemical potential that yield

discontinuous observable properties at  $T_g$ . Two of these properties—specific heat and the coefficient of thermal expansion—have been identified above. The following thermodynamic relations provide a rigorous summary of all discontinuous thermophysical properties at a second order phase transition:

$$\left[ \frac{\partial}{\partial T} \left\{ \frac{\partial \mu}{\partial T} \right\}_{p,p} \right] = - \left\{ \frac{\partial s}{\partial T} \right\}_p = - \frac{C_p}{T}$$

$$\left[ \frac{\partial}{\partial p} \left\{ \frac{\partial \mu}{\partial p} \right\}_{T,T} \right] = \left\{ \frac{\partial v}{\partial p} \right\}_T = -v\beta$$

$$\left[ \frac{\partial}{\partial T} \left\{ \frac{\partial \mu}{\partial p} \right\}_{T,p} \right] = \left\{ \frac{\partial v}{\partial T} \right\}_p = v\alpha$$

where  $\alpha$  is the isobaric coefficient of thermal expansion and  $\beta$  is the isothermal compressibility. Since  $\mu$  is an exact differential, the order of mixed second partial differentiation with respect to  $T$  and  $p$  can be reversed without affecting the final result. Hence, one obtains the third equation above (i.e.,  $v\alpha$ ) upon taking the pressure derivative first, and the temperature derivative second.  $\Delta\alpha$ ,  $\Delta\beta$ , and  $\Delta C_p$  are greater than zero for all materials at  $T_g$ , where  $\Delta$  represents the difference between thermophysical properties in the liquid and glassy states. Even though one typically assumes that liquids are incompressible, liquid state compressibilities are greater than the compressibility of glasses, or amorphous solids. All of the results discussed above are applicable to pure materials and mixtures. Since there are  $r + 1$  degrees of freedom for a single-phase mixture of  $r$  components,  $r + 1$  independent variables are required for a unique description of the chemical potential of component  $i$ . Hence, the rigorous definition of a second-order phase transition stipulates that all of the second partial derivatives of  $\mu_i$  are discontinuous, where  $1 \leq i \leq r$ . For each component, there are  $(r + 1)$  second partial derivatives of  $\mu_i$ , where differentiation is performed twice with respect to the same independent variable (i.e.,  $\partial^2 \mu_i / \partial x_i^2$ , with  $x_i$  representing an independent variable), and  $r(r + 1)$  mixed second partial derivatives (i.e.,  $\partial^2 \mu_i / \partial x_j \partial x_k$ ,  $j \neq k$ ). Since the order of mixed second partial differentiation can be reversed without affecting the final result, there are  $r(r + 1)/2$  mixed second partial derivatives of each  $\mu_i$  that yield useful independent information. Most of these discontinuous quantities can be expressed in terms of the concentration dependence of (i) partial molar volume, (ii) partial molar entropy, and (iii) the chemical potential of each component. In summary, there are  $(r + 1)(1 + r/2)$  discontinuous thermophysical properties at  $T_g$  per component, and the total number of discontinuous quantities for a mixture of  $r$  components is

$$r(r + 1)(1 + r/2)$$

As expected, this analysis indicates that there are three discontinuous observables for a pure material (i.e.,  $r = 1$ ).

### 1.3 THE EQUILIBRIUM GLASSY STATE

Most glasses are not in a state of thermodynamic equilibrium. In fact, one can argue that the glass transition is not an equilibrium second-order phase transition because the measured value of  $T_g$  depends on the experimental rate of heating or cooling. If a viscous liquid achieves thermodynamic equilibrium above  $T_g$  and the temperature decreases at an infinitesimally slow rate, then conformational rearrangements of the chain backbone via rotation about carbon–carbon single bonds should allow the material to contract macroscopically on a time scale that is on the order of, or faster than, the experimental cooling rate. Under these conditions, the system traverses a sequence of equilibrium states and the coefficient of thermal expansion should decrease abruptly upon cooling at the equilibrium glass transition. Simple volume–temperature calculations reveal that this hypothetical “equilibrium glassy state” exists, and that  $\alpha$  decreases abruptly at  $T_{g, \text{equil}}$  when materials are cooled at an infinitesimally slow rate. If one assumes typical values for specific volume of hydrocarbon polymers (i.e.,  $\rho \approx 1.2 \text{ g/cm}^3$ ) and the coefficient of thermal expansion of a common liquid at ambient conditions (i.e.,  $\alpha_{\text{Liquid}} \approx 5\text{--}6 \times 10^{-4} \text{ K}^{-1}$ ), and extrapolates the liquidus line to 0 K at a slope dictated by  $\alpha_{\text{Liquid}}$ ,

$$v(T) = v(T_{\text{reference}}) \exp\{\alpha_{\text{Liquid}}(T - T_{\text{reference}})\}$$

$$T_{\text{reference}} = 300 \text{ K}$$

$$v(T_{\text{reference}}) = \frac{1}{1.2 \text{ g/cm}^3}$$

$$\alpha_{\text{Liquid}} \approx (5\text{--}6) \times 10^{-4} \text{ K}^{-1}$$

then predictions yield unacceptably low specific volume at absolute zero. This anomaly is prevented if  $\alpha$  decreases when materials are cooled below  $T_g$ . Hence, the following theorem summarizes these observations:

There must be an equilibrium glass transition temperature  $T_{g, \text{equil}}$  below which  $\alpha_{\text{Glass}} < \alpha_{\text{Liquid}}$ . Otherwise, equilibrium liquidus volume–temperature curves extrapolate to unrealistically low volume at absolute zero. The slope of the volume–temperature curve must exhibit a discontinuity at  $T_{g, \text{equil}}$  when experiments are conducted on an infinite time scale. In practice, finite rates of heating or cooling are required to measure  $T_g$ , and these kinetic measurements yield pseudo-phase-transition temperatures that are greater than  $T_{g, \text{equil}}$ .

### 1.4 PHYSICAL AGING, DENSIFICATION, AND VOLUME AND ENTHALPY RELAXATION

Comments from the previous section provide support for the existence of an equilibrium glassy state that can be discussed in principle, but never achieved in practice. This is equivalent to the well-known phenomenon in heat transfer where the temperature of fluids moving through heat exchangers can approach but never achieve the

temperature of the surroundings unless the area of the exchanger is infinitely large or the flow rate is infinitesimally slow. Materials are aware of the specific volume and enthalpy that they might achieve as equilibrium glasses. The difference between their nonequilibrium and equilibrium properties provides the driving force for volume and enthalpy relaxation. The former is also known as densification or physical aging. Enthalpy relaxation affects the shape of a calorimeter trace during subsequent heating segments. For example, upon heating in the vicinity of the glass transition, one observes the superposition of a second-order phase transition (as expected for amorphous materials) and a first-order phase transition as materials recover from the decrease in specific enthalpy that occurred below  $T_g$  during relaxation toward the equilibrium glassy state. This type of response for  $C_p$  versus  $T$  occurs, to some extent, because glasses exhibit time-dependent (i.e., kinetic) behavior under experimental conditions. One does not follow the same sequence of nonequilibrium states upon heating and cooling amorphous materials in the vicinity of the glass transition temperature when kinetic processes occur below  $T_g$  that produce densified glasses. When an equilibrium liquid densifies via slow cooling, the material follows a sequence of states that exhibit reduced volume according to  $\alpha_{\text{Liquid}}$ , and this behavior continues to much lower temperature relative to the sequence of states that is traversed at faster cooling. Hence, the glass transition temperature is lower when cooling occurs at a slower rate, and the glass that forms is densified relative to glasses that form at faster cooling rates. Now, when less dense glasses, that are produced at faster cooling rates, relax to a densified glass, the heating trace for this densified glass follows a different set of states in the vicinity of  $T_g$  relative to the sequence of states that is traversed from the liquid phase when this densified glass is formed upon cooling. The densified glass that forms via slower cooling from the liquid state reveals a lower  $T_g$ . In contrast, when nonequilibrium densified glasses form via enthalpy and volume relaxation from a less dense glass, the heating traces for these densified glasses reveal a  $T_g$  (upon heating) that exceeds  $T_g$  (upon cooling) for the less dense glass. In general, densified glasses exhibit more restricted mobility and reduced fractional free volume relative to less dense glasses, and this morphological difference is reflected in the measurement of  $T_g$  upon heating because materials must achieve a certain level of chain mobility, including translation and reptation of the backbone, before one observes a second-order transition to the viscous liquid state. Enthalpy relaxation effects on differential scanning calorimetry (DSC) heating traces are most prominent when materials are held isothermally in the glassy state, approximately 20–50 °C below  $T_g$ , for a significant duration of time. Above  $T_g$ , material behavior follows a sequence of equilibrium liquid states that do not depend on heating or cooling rates. Below  $T_g$ , experimental cooling rates, defined by  $r = -dT/dt$ , affect the magnitude of the driving force for volume and enthalpy relaxation, as illustrated below:

#### Volume relaxation

$$\text{Driving force} = v(T; r) - v_{\text{equilibrium}}(T)$$

#### Enthalpy relaxation

$$\text{Driving force} = h(T; r) - h_{\text{equilibrium}}(T)$$

If conformational rearrangements of a single polymer chain have a strong influence on macroscopic volume, then higher rates of cooling produce a glass with larger specific volume because the rate of volume contraction becomes sluggish at lower temperature and occurs on a time scale that is much longer than the experimental cooling rate. In other words, materials that undergo thermal contraction according to  $\alpha_{\text{Liquid}}$  along the equilibrium liquidus line, experience a glass transition at higher temperature when the cooling rate increases. Now, thermal contraction during further cooling follows  $\alpha_{\text{Glass}}$ . Hence, the driving force for volume (and enthalpy) relaxation below  $T_g$  increases at higher cooling rates. On the other hand, the sluggishness of volume contraction at lower temperature is consistent with a decrease in mobility, which causes volume and enthalpy relaxation to occur at a slower rate. Temperature and cooling rate produce competing effects on relaxation processes because faster cooling increases the driving force, but materials are usually cooled to lower temperatures at higher rates of cooling, which decrease mobility. Qualitatively, it is acceptable to envision these relaxation processes as a product of (i) temperature-dependent mobility and (ii) temperature- and rate-dependent driving force.

## 1.5 TEMPERATURE–PRESSURE DIFFERENTIAL PHASE EQUILIBRIUM RELATIONS FOR FIRST-ORDER PROCESSES: THE CLAPEYRON EQUATION

The statement of chemical equilibrium for pure materials is useful to develop phase coexistence relations. The integral approach to phase equilibrium is based on

$$\mu_{\text{Solid}}(T_m^-) = \mu_{\text{Liquid}}(T_m^+)$$

whereas the differential approach,

$$d\mu_{\text{Solid}}(T_m^-) = d\mu_{\text{Liquid}}(T_m^+)$$

is the method of choice to calculate the pressure dependence of  $T_m$  via the Clapeyron equation. The final result is also valid for mixtures because the pressure dependence of  $T_g$  is evaluated at constant composition. The Gibbs–Duhem equation (i.e., see Section 1.2) is employed to express the total differential of the chemical potential in terms of temperature and pressure. For example,

$$-s_{\text{Solid}} dT_{\text{Solid}} + v_{\text{Solid}} dp_{\text{Solid}} = -s_{\text{Liquid}} dT_{\text{Liquid}} + v_{\text{Liquid}} dp_{\text{Liquid}}$$

implies that differential changes in  $\mu_{\text{Solid}}$  and  $\mu_{\text{Liquid}}$  must be balanced along the solid–liquid boundary on a temperature–pressure phase diagram. Differential statements of thermal and mechanical equilibrium in the absence of external fields are

$$\begin{aligned} dT_{\text{Solid}} &= dT_{\text{Liquid}} \\ dp_{\text{Solid}} &= dp_{\text{Liquid}} \end{aligned}$$

The latter statement of mechanical equilibrium must be modified if an external field is present. For example, when external fields exert a species-specific force on each component in a mixture (i.e.,  $N$  components), the statements of thermal and chemical equilibrium require that temperature and field-dependent chemical potential gradients

must vanish (i.e.,  $\nabla T = 0$ ,  $\nabla \mu_i = 0$  for  $1 \leq i \leq N$ ), but the Gibbs–Duhem equation yields the following result for the pressure gradient:

$$\nabla p = - \sum_{i=1}^N \rho_i \nabla \varphi_i$$

where  $\rho_i$  is the mass density of species  $i$  in the mixture and  $\varphi_i$  is the specific external potential with dimensions of energy per mass that exerts force  $\nabla \varphi_i$  on the  $i$ th component. In a gravitational field where all species experience the same force, the specific external potential  $\varphi$  is given by the product of the gravitational acceleration constant  $g$  and a position variable that increases vertically upward (i.e., opposite to the gravitational acceleration vector). Now, the pressure gradient is balanced by the gravitational force,  $\nabla p = \rho \mathbf{g}$ , which is consistent with the momentum balance under hydrostatic conditions. The statement of complete thermodynamic solid–liquid equilibrium for simple systems in the absence of external force fields with no gradients in temperature, pressure, or chemical potential yields the following relation between temperature and pressure along a solid–liquid phase boundary:

$$\left\{ \frac{\partial T}{\partial p} \right\}_{@T_{\text{melt}}} = \frac{v_{\text{Liquid}} - v_{\text{Solid}}}{s_{\text{Liquid}} - s_{\text{Solid}}} = \frac{\Delta v_{\text{melt}}}{\Delta s_{\text{melt}}}$$

This is the Clapeyron equation for first-order solid–liquid phase transitions, and it applies to any two phases in equilibrium that exhibit discontinuities in the first derivatives of the chemical potential at the transition temperature. Since  $\Delta v_{\text{melt}}$  and  $\Delta s_{\text{melt}}$  represent two discontinuous thermophysical properties at  $T_m$  that increase abruptly as materials are heated from the solid state to the liquid state, it is generally true that  $T_m$  is higher when the pressure increases. However, the melting temperature decreases at higher pressure for  $\text{H}_2\text{O}$  because  $\Delta v_{\text{melt}}$  is negative (i.e., the liquid phase slightly above  $T_m$  is more dense than the solid phase slightly below  $T_m$ ). The Clapeyron equation does not yield useful information for a second-order thermodynamic phase transition because volume and entropy are continuous at  $T_g$ . If one differentiates numerator and denominator of the Clapeyron equation (i) with respect to temperature at constant pressure and then (ii) with respect to pressure at constant temperature, it is possible to generate two Ehrenfest equations that predict the pressure dependence of  $T_g$  [Ehrenfest, 1933; Goldstein, 1963]. The first approach is equivalent to invoking entropy continuity at  $T_g$ , and the second approach is equivalent to invoking volume continuity at  $T_g$ .

## 1.6 TEMPERATURE–PRESSURE DIFFERENTIAL PHASE EQUILIBRIUM RELATIONS FOR SECOND-ORDER PROCESSES: THE EHRENFEST EQUATIONS

### 1.6.1 Volume Continuity

The pressure dependence of  $T_g$  is developed by expressing the specific volume of the liquid and the glass in terms of  $T$  and  $p$  for a pure material. This is sufficient for

two-phase equilibrium of pure materials because there are two degrees of freedom, and  $T$  and  $p$  can be chosen independently in each separate phase. The final results are also valid for mixtures because one can focus on the relation between temperature and pressure changes along the glass–liquid phase boundary at constant composition. The integral approach to volume continuity at  $T_g$  for a pure material is based on

$$v_{\text{Glass}}(T, p) = v_{\text{Liquid}}(T, p)$$

and the differential approach begins with the following statement:

$$dv_{\text{Glass}}(T, p) = dv_{\text{Liquid}}(T, p)$$

Since temperature and pressure must be the same in each phase, unless strong external fields are present, the differential statement of volume continuity becomes

$$\left\{ \frac{\partial v_{\text{Glass}}}{\partial T} \right\}_p dT + \left\{ \frac{\partial v_{\text{Glass}}}{\partial p} \right\}_T dp = \left\{ \frac{\partial v_{\text{Liquid}}}{\partial T} \right\}_p dT + \left\{ \frac{\partial v_{\text{Liquid}}}{\partial p} \right\}_T dp$$

Now, the temperature and pressure coefficients of specific volume are expressed in terms of volumetric thermal expansion and isothermal compressibility, respectively:

$$\left\{ \frac{\partial v}{\partial T} \right\}_p = v\alpha; \quad \left\{ \frac{\partial v}{\partial p} \right\}_T = -v\beta$$

Hence,

$$v_{\text{Glass}}\alpha_{\text{Glass}} dT - v_{\text{Glass}}\beta_{\text{Glass}} dp = v_{\text{Liquid}}\alpha_{\text{Liquid}} dT - v_{\text{Liquid}}\beta_{\text{Liquid}} dp$$

There is only one degree of freedom for two-phase equilibrium of a pure material, and the previous restriction indicates that temperature and pressure changes are not independent on the glass transition phase boundary. Since  $v_{\text{Glass}} = v_{\text{Liquid}}$ , the differential relation between  $T$  and  $p$  along a glass–liquid boundary is

$$\left\{ \frac{\partial T}{\partial p} \right\}_{@T_{\text{glass}}} = \frac{\beta_{\text{Liquid}} - \beta_{\text{Glass}}}{\alpha_{\text{Liquid}} - \alpha_{\text{Glass}}} = \frac{\Delta\beta}{\Delta\alpha}$$

As mentioned earlier, this Ehrenfest equation is equivalent to applying l'Hôpital's rule to the Clapeyron equation via differentiation with respect to pressure at constant temperature. Since liquids are more compressible and thermally more expandable than glasses,  $T_g$  increases invariably at higher pressure (i.e., by about 20–30 °C per kilobar). There are no exceptions to this rule. Typical values for the discontinuity in thermal expansion and isothermal compressibility at the glass transition temperature are  $5 \times 10^{-4} \text{ K}^{-1}$  for  $\Delta\alpha$  and  $1 \times 10^{-5} \text{ atm}^{-1}$  for  $\Delta\beta$ . Dense glasses are produced when molten polymers in the highly viscous liquid state are subjected to high pressure and cooled below  $T_g$ . This densified amorphous structure is essentially “frozen” upon cooling below the glass transition temperature. However, materials lose all memory of prior processing history when they are heated above  $T_g$  in a differential scanning calorimeter at ambient pressure.

### 1.6.2 Entropy Continuity

If one invokes entropy continuity at  $T_g$  via the differential approach to two-phase equilibrium, then another Ehrenfest equation describes the pressure dependence of  $T_g$ . Once again,  $T$  and  $p$  represent two independent variables for a complete description of pure-component specific entropies in the liquid and glassy states. Hence,

$$\begin{aligned}s_{\text{Glass}}(T, p) &= s_{\text{Liquid}}(T, p) \\ ds_{\text{Glass}}(T, p) &= ds_{\text{Liquid}}(T, p)\end{aligned}$$

and the differential statement of entropy continuity at  $T_g$  becomes

$$\left\{ \frac{\partial s_{\text{Glass}}}{\partial T} \right\}_p dT + \left\{ \frac{\partial s_{\text{Glass}}}{\partial p} \right\}_T dp = \left\{ \frac{\partial s_{\text{Liquid}}}{\partial T} \right\}_p dT + \left\{ \frac{\partial s_{\text{Liquid}}}{\partial p} \right\}_T dp$$

The temperature and pressure coefficients of specific entropy are

$$\begin{aligned}\left\{ \frac{\partial s}{\partial T} \right\}_p &= \frac{C_p}{T} \\ \left\{ \frac{\partial s}{\partial p} \right\}_T &= - \left\{ \frac{\partial v}{\partial T} \right\}_p = -v\alpha\end{aligned}$$

The temperature coefficient of  $s$  at constant pressure is based on the total differential of specific enthalpy:

$$dh = T ds + v dp + \text{composition-dependent terms for mixtures}$$

and the definition of specific heat,  $C_p = (\partial h / \partial T)_{p, \text{composition}}$ . The pressure coefficient of specific entropy at constant temperature is derived from a Maxwell relation using the Gibbs potential:

$$dg = -s dT + v dp + \text{composition-dependent terms for mixtures}$$

because the order of mixed second partial differentiation can be reversed without affecting the final result since  $g$  is a state function (i.e., exact differential). Hence,

$$C_{p, \text{Glass}} d \ln T - v_{\text{Glass}} \alpha_{\text{Glass}} dp = C_{p, \text{Liquid}} d \ln T - v_{\text{Liquid}} \alpha_{\text{Liquid}} dp$$

The phase rule for glass–liquid equilibrium of a pure material indicates that fluctuations in  $T$  and  $p$  cannot occur independently. As one traverses the two-phase boundary between the liquid and glassy states, differential changes in  $T$  and  $p$  must follow:

$$\left\{ \frac{\partial \ln T_g}{\partial p} \right\}_{\text{constant composition}} = \frac{v_{\text{Liquid}} \alpha_{\text{Liquid}} - v_{\text{Glass}} \alpha_{\text{Glass}}}{C_{p, \text{Liquid}} - C_{p, \text{Glass}}}$$

Since volume continuity at  $T_g$  requires that  $v_{\text{Glass}} = v_{\text{Liquid}}$ , the previous expression reduces to

$$\left\{ \frac{\partial \ln T_g}{\partial p} \right\}_{\text{constant composition}} = \frac{v \Delta \alpha}{\Delta C_p}$$

where the discontinuity in specific heat (i.e.,  $\Delta C_p$ ) at the glass transition temperature is approximately 0.2–0.3 J/(g·K). Volume and entropy continuity at a second-order thermodynamic phase transition yield two Ehrenfest equations for the pressure dependence of  $T_g$ . These are summarized below.

$$\left\{ \frac{\partial T_g}{\partial p} \right\}_{\text{constant composition}} = \frac{\Delta \beta}{\Delta \alpha} \quad (1.1)$$

$$\left\{ \frac{\partial T_g}{\partial p} \right\}_{\text{constant composition}} = \frac{v T_g \Delta \alpha}{\Delta C_p} \quad (1.2)$$

Division of Eq. (1.1) by (1.2) yields the Prigogine–Defay ratio, which should approach unity based on volume and entropy continuity at the glass transition [Prigogine and Defay, 1954]. However, when two order parameters are required to describe the morphological structure of glasses at an equilibrium second-order phase transition, the developments in Chapter 5 reveal that predictions from Eq. (1.1) yield a larger pressure dependence of  $T_g$  relative to Eq. (1.2). Now, the Prigogine–Defay ratio exceeds unity, and entropy continuity provides a better estimate of the pressure dependence of  $T_g$ , given by Eq. (1.2) above. If the discontinuous thermophysical properties at  $T_g$  are very weak functions of pressure, then the Ehrenfest equations can be integrated to predict  $T_g$  at different pressures:

$$T_g(p) \approx T_g(p_{\text{reference}}) + \frac{\Delta \beta}{\Delta \alpha} (p - p_{\text{reference}}) \quad (1.3)$$

$$T_g(p) \approx T_g(p_{\text{reference}}) \exp \left\{ \frac{(p - p_{\text{reference}}) v_{p_{\text{reference}}} \Delta \alpha}{\Delta C_p} \right\} \quad (1.4)$$

If one accounts for the pressure dependence of specific volume via the coefficient of isothermal compressibility as follows:

$$\left\{ \frac{\partial \ln v}{\partial p} \right\}_T = -\beta$$

$$v(p) \approx v(p_{\text{reference}}) \exp\{-\beta(p - p_{\text{reference}})\}$$

then Ehrenfest equation (1.2) in differential form, based on entropy continuity, is written as

$$\Delta C_p \left\{ \frac{\partial \ln T_g}{\partial p} \right\}_{\text{constant composition}} \approx \frac{\alpha_{\text{Liquid}} v_{\text{Liquid}}(p_{\text{reference}}) \exp\{-\beta_{\text{Liquid}}(p - p_{\text{reference}})\}}{-\alpha_{\text{Glass}} v_{\text{Glass}}(p_{\text{reference}}) \exp\{-\beta_{\text{Glass}}(p - p_{\text{reference}})\}}$$

## 1.7 COMPOSITIONAL DEPENDENCE OF $T_g$ VIA ENTROPY CONTINUITY

Glass transition temperature measurements can be used as a diagnostic probe of the phase behavior of mixtures. Completely miscible blends exhibit only one concentration-dependent  $T_g$ . If phase separation occurs, then a different  $T_g$  is characteristic of each phase. The formalism presented in this section applies to polymer–polymer and polymer–diluent blends, as well as random copolymers, which are considered to be miscible. Diluents can be plasticizers, antiplasticizers, ultraviolet stabilizers, antioxidants, dissolved supercritical  $\text{CO}_2$ , and so on. Most practical applications involve binary or ternary blends. However, completely miscible multicomponent systems are addressed later. The total specific entropy of a mixture of  $r$  components is expressed as a weight-fraction-weighted sum of pure-component specific entropies for each component, and a contribution due to the mixing process. The total specific entropy of the liquid at the mixture  $T_g$  is

$$s_{\text{total,Liquid}}(T_{g,\text{mixture}}) = \sum_{i=1}^r \omega_{i,\text{Liquid}} s_{i,\text{Liquid}}(T_{g,\text{mixture}}) + \Delta s_{\text{mixing,Liquid}}(T_{g,\text{mixture}})$$

where  $\omega_{i,\text{Liquid}}$  is the mass fraction of component  $i$  in the equilibrium liquid phase,  $s_{i,\text{Liquid}}$  is the pure-component specific entropy of component  $i$ , and  $\Delta s_{\text{mixing,Liquid}}$  is the conformational entropy change due to mixing, which is best described in terms of lattice theories (i.e., Flory–Huggins, Guggenheim, Stavermann, Sanchez–Lacombe, etc.) according to Chapter 3. The total specific entropy of the glass at the mixture  $T_g$  is

$$s_{\text{total,Glass}}(T_{g,\text{mixture}}) = \sum_{i=1}^r \omega_{i,\text{Glass}} s_{i,\text{Glass}}(T_{g,\text{mixture}}) + \Delta s_{\text{mixing,Glass}}(T_{g,\text{mixture}})$$

where all variables described above in the liquid state have similar definitions in the glassy state. The mixture is ideal with partition coefficients of unity because it is assumed that the mass fraction of component  $i$  is the same in both phases. Hence,

$$\omega_{i,\text{Glass}} = \omega_{i,\text{Liquid}} = \omega_i$$

One typically equates the chemical potential of component  $i$  in both phases and develops relations between concentration variables in the corresponding phases at equilibrium. This tedium is circumvented by assuming ideality and the equality of component  $i$ 's mass fraction in both phases. Entropy continuity is invoked at  $T_{g,\text{mixture}}$  and the conformational entropy of mixing is assumed to be the same in the liquid and glassy states at the mixture  $T_g$ . Hence,

$$\begin{aligned} s_{\text{total,Liquid}}(T_{g,\text{mixture}}) &= s_{\text{total,Glass}}(T_{g,\text{mixture}}) \\ \Delta s_{\text{mixing,Liquid}}(T_{g,\text{mixture}}) &= \Delta s_{\text{mixing,Glass}}(T_{g,\text{mixture}}) \\ \sum_{i=1}^r \omega_i \{ s_{i,\text{Liquid}}(T_{g,\text{mixture}}) - s_{i,\text{Glass}}(T_{g,\text{mixture}}) \} &= 0 \end{aligned}$$

If second-order equilibrium phase transitions occur at constant pressure, which could be controversial, then the temperature dependence of specific entropy is evaluated using the total differential of specific enthalpy:

$$dh = T ds + v dp + \text{composition-dependent terms for mixtures}$$

At constant pressure and composition,

$$\left\{ \frac{\partial h}{\partial T} \right\}_{p, \text{composition}} = C_p = T \left\{ \frac{\partial s}{\partial T} \right\}_{p, \text{composition}}$$

The specific entropy of component  $i$  is evaluated with respect to reference temperature,  $T_{\text{reference}}$ :

$$s_{i, \text{Liquid}}(T_{g, \text{mixture}}) = s_{i, \text{Liquid}}(T_{\text{reference}}) + \int_{T_{\text{reference}}}^{T_{g, \text{mixture}}} C_{pi, \text{Liquid}} d \ln T$$

$$s_{i, \text{Glass}}(T_{g, \text{mixture}}) = s_{i, \text{Glass}}(T_{\text{reference}}) + \int_{T_{\text{reference}}}^{T_{g, \text{mixture}}} C_{pi, \text{Glass}} d \ln T$$

For temperature-independent specific heats, or temperature-averaged values of  $C_p$ , the two previous equations are simplified as follows:

$$s_{i, \text{Liquid}}(T_{g, \text{mixture}}) = s_{i, \text{Liquid}}(T_{\text{reference}}) + C_{pi, \text{Liquid}} \ln \left\{ \frac{T_{g, \text{mixture}}}{T_{\text{reference}}} \right\}$$

$$s_{i, \text{Glass}}(T_{g, \text{mixture}}) = s_{i, \text{Glass}}(T_{\text{reference}}) + C_{pi, \text{Glass}} \ln \left\{ \frac{T_{g, \text{mixture}}}{T_{\text{reference}}} \right\}$$

$T_{\text{reference}}$  is chosen as the glass transition temperature of pure component  $i$ ,  $T_{g, i}$ . Furthermore, entropy continuity is invoked for each pure component at  $T_{g, i}$ :

$$s_{i, \text{Liquid}}(T_{g, i}) = s_{i, \text{Glass}}(T_{g, i})$$

Hence,

$$s_{i, \text{Liquid}}(T_{g, \text{mixture}}) - s_{i, \text{Glass}}(T_{g, \text{mixture}}) = \Delta C_{pi} \ln \left\{ \frac{T_{g, \text{mixture}}}{T_{g, i}} \right\}$$

where  $\Delta C_{pi}$  is the discontinuous increment in specific heat (i.e.,  $C_{pi, \text{Liquid}} - C_{pi, \text{Glass}}$ ) of component  $i$  at its pure-component glass transition temperature,  $T_{g, i}$ . Entropy continuity for a multicomponent mixture at  $T_{g, \text{mixture}}$  yields

$$\sum_{i=1}^r \omega_i \Delta C_{pi} \ln \left\{ \frac{T_{g, \text{mixture}}}{T_{g, i}} \right\} = 0$$

Rearrangement of the previous equation allows one to predict the mixture  $T_g$  in terms of composition variables and pure-component thermophysical properties:

$$\ln\{T_{g,\text{mixture}}\} = \frac{\sum_{i=1}^r \omega_i \Delta C_{pi} \ln\{T_{g,i}\}}{\sum_{i=1}^r \omega_i \Delta C_{pi}}$$

This is the Couchman–Karasz equation for the compositional dependence of the glass transition temperature in miscible multicomponent mixtures via entropy continuity [Couchman and Karasz, 1978]. Most  $T_g$ –composition relations for miscible mixtures can be obtained from the Couchman–Karasz equation by invoking additional approximations or assumptions. This is illustrated below for the classic Gordon–Taylor and Fox equations. For example, if component  $k$  is chosen arbitrarily, then

$$\begin{aligned} \ln\{T_{g,\text{mixture}}\} - \ln\{T_{g,k}\} &= \frac{\sum_{i=1}^r \omega_i \Delta C_{pi} [\ln\{T_{g,i}\} - \ln\{T_{g,k}\}]}{\sum_{i=1}^r \omega_i \Delta C_{pi}} \\ \ln\left\{\frac{T_{g,\text{mixture}}}{T_{g,k}}\right\} &= \frac{\sum_{i=1}^r \omega_i \Delta C_{pi} \ln\left\{\frac{T_{g,i}}{T_{g,k}}\right\}}{\sum_{i=1}^r \omega_i \Delta C_{pi}} \end{aligned}$$

Even though  $T_{g,\text{mixture}}$  and  $T_{g,k}$  are different, if an absolute temperature scale is employed, as required, then the ratio of  $T_{g,\text{mixture}}$  to  $T_{g,k}$  is not very different from unity. Hence, it is acceptable to expand the log of the  $T_g$  ratios on each side of the previous equation and truncate the series after the linear term. In other words,

$$\begin{aligned} T_{g,\text{mixture}} &= T_{g,k} + \Delta T_{g,\text{mix}/k} \\ \varepsilon &= \frac{\Delta T_{g,\text{mix}/k}}{T_{g,k}} = \frac{T_{g,\text{mixture}}}{T_{g,k}} - 1 \\ \ln\left\{\frac{T_{g,\text{mixture}}}{T_{g,k}}\right\} &= \ln(1 + \varepsilon) \approx \varepsilon = \frac{T_{g,\text{mixture}}}{T_{g,k}} - 1 \end{aligned}$$

Similarly,

$$\ln\left\{\frac{T_{g,i}}{T_{g,k}}\right\} \approx \frac{T_{g,i}}{T_{g,k}} - 1$$

The previous two approximations for the *logarithm* of a temperature ratio are used to arrive at the Gordon–Taylor equation for the compositional dependence of  $T_{g,\text{mixture}}$ :

$$\frac{T_{g,\text{mixture}}}{T_{g,k}} - 1 = \frac{\sum_{i=1}^r \omega_i \Delta C_{pi} \left\{\frac{T_{g,i}}{T_{g,k}} - 1\right\}}{\sum_{i=1}^r \omega_i \Delta C_{pi}}$$

The final result predicts curvature in  $T_{g,\text{mixture}}$  versus composition for binary mixtures:

$$T_{g,\text{mixture}} = \frac{\sum_{i=1}^r \omega_i \Delta C_{pi} T_{g,i}}{\sum_{i=1}^r \omega_i \Delta C_{pi}}$$

The following assumptions were invoked to derive the Gordon–Taylor equation:

- (a) Entropy continuity:  $s_{i,\text{Liquid}}(T_{g,i}) = s_{i,\text{Glass}}(T_{g,i})$   
 $s_{\text{total,Liquid}}(T_{g,\text{mixture}}) = s_{\text{total,Glass}}(T_{g,\text{mixture}})$   
 $\Delta s_{\text{mixing,Liquid}}(T_{g,\text{mixture}}) = \Delta s_{\text{mixing,Glass}}(T_{g,\text{mixture}})$
- (b) Ideal mixtures:  $\omega_{i,\text{Glass}} = \omega_{i,\text{Liquid}}$
- (c) Upon heating,  $T_g$  occurs at constant pressure.
- (d) Temperature-independent pure-component specific heats:

$$C_{pi,\text{Liquid}} \neq f(T)$$

$$C_{pi,\text{Glass}} \neq f(T)$$

(e)  $\ln \left\{ \frac{T_{g,i}}{T_{g,k}} \right\} \approx \frac{T_{g,i}}{T_{g,k}} - 1 + \dots$

If the following assumption is included in the previous list,

- (f<sub>1</sub>)  $T_{g,i} \Delta C_{pi}(@ T_{g,i})$  is a constant that is the same for all components

then the Gordon–Taylor equation reduces to the Fox equation:

$$\frac{1}{T_{g,\text{mixture}}} = \sum_{i=1}^r \frac{\omega_i}{T_{g,i}}$$

which only requires knowledge of pure-component glass transition temperatures and the mixture composition. The Fox equation predicts curvature in  $T_{g,\text{mixture}}$  versus composition for binary mixtures (see Problem 1.10d and Figure 1.1). If assumption (f<sub>1</sub>) is replaced by

- (f<sub>2</sub>)  $\Delta C_{pi}(@ T_{g,i})$  is a constant that is the same for all components

then the Gordon–Taylor equation reduces to the following *additive rule of mixtures* (i.e., linear weight-fraction-weighted sum of pure-component glass transition temperatures), which does not predict curvature in the compositional dependence of  $T_{g,\text{mixture}}$ :

$$T_{g,\text{mixture}} = \sum_{i=1}^r \omega_i T_{g,i}$$

## 1.8 COMPOSITIONAL DEPENDENCE OF $T_g$ VIA VOLUME CONTINUITY

A modified version of the Gordon–Taylor equation is developed by invoking volume continuity of each component and the mixture at their respective glass transition temperatures. The specific volume of the liquid mixture at  $T_{g,\text{mixture}}$  is calculated as a volume-fraction-weighted sum of pure-component specific volumes, and the volume change due to mixing;

$$v_{\text{total,Liquid}}(T_{g,\text{mixture}}) = \sum_{i=1}^r \{\varphi_i v_{i,\text{Liquid}}(T_{g,\text{mixture}})\} + \Delta v_{\text{mixing,Liquid}}(T_{g,\text{mixture}})$$

where  $\varphi_i$  is the volume fraction of component  $i$  in both phases,  $v_{i,\text{Liquid}}$  is the specific volume of pure component  $i$ , and  $\Delta v_{\text{mixing,Liquid}}$  is the volume change upon mixing due to conformational changes and energetic interactions in the equilibrium liquid. Likewise, the specific volume of the glass at  $T_{g,\text{mixture}}$  is calculated as follows:

$$v_{\text{total,Glass}}(T_{g,\text{mixture}}) = \sum_{i=1}^r \{\varphi_i v_{i,\text{Glass}}(T_{g,\text{mixture}})\} + \Delta v_{\text{mixing,Glass}}(T_{g,\text{mixture}})$$

If second-order phase transitions occur at constant pressure, then the following equation is integrated with the assumption that thermal expansion coefficients are essentially independent of temperature or specific volume:

$$\alpha = \left\{ \frac{\partial \ln v}{\partial T} \right\}_p$$

The reference temperature for component  $i$  is its pure-component glass transition,  $T_{g,i}$ . Hence,

$$\begin{aligned} v_{i,\text{Liquid}}(T) &\approx v_{i,\text{Liquid}}(T_{g,i}) \exp\{\alpha_{i,\text{Liquid}}(T - T_{g,i})\} \\ v_{i,\text{Glass}}(T) &\approx v_{i,\text{Glass}}(T_{g,i}) \exp\{\alpha_{i,\text{Glass}}(T - T_{g,i})\} \end{aligned}$$

Now, one invokes volume continuity of the mixture at  $T_{g,\text{mixture}}$  and assumes that volume changes upon mixing are the same for the equilibrium liquid and glass. Hence,

$$\begin{aligned} v_{\text{total,Liquid}}(T_{g,\text{mixture}}) &= v_{\text{total,Glass}}(T_{g,\text{mixture}}) \\ \Delta v_{\text{mixing,Liquid}}(T_{g,\text{mixture}}) &= \Delta v_{\text{mixing,Glass}}(T_{g,\text{mixture}}) \end{aligned}$$

The result is

$$\begin{aligned} &\sum_{i=1}^r \varphi_i v_{i,\text{Liquid}}(T_{g,i}) \exp\{\alpha_{i,\text{Liquid}}(T_{g,\text{mixture}} - T_{g,i})\} \\ &= \sum_{i=1}^r \varphi_i v_{i,\text{Glass}}(T_{g,i}) \exp\{\alpha_{i,\text{Glass}}(T_{g,\text{mixture}} - T_{g,i})\} \end{aligned}$$

The exponentials are expanded in a Taylor series and truncation is performed after the linear terms. This is reasonable because thermal expansion coefficients are on the order of  $5 \times 10^{-4} \text{ K}^{-1}$ . Since temperatures are in the 300–500 K range, the argument of each exponential is between 0.15 and 0.25. Under these conditions,

$$\exp\{\alpha_i(T_{g,\text{mixture}} - T_{g,i})\} \approx 1 + \alpha_i(T_{g,\text{mixture}} - T_{g,i}) + \dots$$

Volume continuity of the mixture assumes the following form:

$$\begin{aligned} &\sum_{i=1}^r \varphi_i v_{i,\text{Liquid}}(T_{g,i}) \{1 + \alpha_{i,\text{Liquid}}(T_{g,\text{mixture}} - T_{g,i})\} \\ &\approx \sum_{i=1}^r \varphi_i v_{i,\text{Glass}}(T_{g,i}) \{1 + \alpha_{i,\text{Glass}}(T_{g,\text{mixture}} - T_{g,i})\} \end{aligned}$$

Since volume continuity of pure component  $i$  at  $T_{g,i}$  is also operative,

$$v_{i,\text{Liquid}}(T_{g,i}) = v_{i,\text{Glass}}(T_{g,i}) = v_i(T_{g,i})$$

one obtains

$$\sum_{i=1}^r \varphi_i v_i(T_{g,i}) \{\alpha_{i,\text{Liquid}} - \alpha_{i,\text{Glass}}\} \{T_{g,\text{mixture}} - T_{g,i}\} \approx 0$$

Hence, one predicts the compositional dependence of  $T_{g,\text{mixture}}$  via the following *volume continuity* modification of the Gordon–Taylor equation for miscible  $r$ -component mixtures:

$$T_{g,\text{mixture}} = \frac{\sum_{i=1}^r \varphi_i T_{g,i} v_{i@T_{g,i}} \Delta\alpha_{i@T_{g,i}}}{\sum_{i=1}^r \varphi_i v_{i@T_{g,i}} \Delta\alpha_{i@T_{g,i}}}$$

where volume fractions  $\varphi_i$  replace weight fractions  $\omega_i$  and the discontinuous increment in thermal expansion coefficient,  $\Delta\alpha_i = \alpha_{i,\text{Liquid}} - \alpha_{i,\text{Glass}}$ , for pure component  $i$  at  $T_{g,i}$  replaces  $\Delta C_{pi}$ .

## 1.9 LINEAR LEAST SQUARES ANALYSIS OF THE GORDON–TAYLOR EQUATION AND OTHER $T_g$ -COMPOSITION RELATIONS FOR BINARY MIXTURES

The original Gordon–Taylor equation for multicomponent mixtures, with  $\ln T_g$  replaced by  $T_g$ ,

$$T_{g,\text{mixture}} = \frac{\sum_{i=1}^r \omega_i \{\Delta C_{p,i@T_{g,i}}\} T_{g,i}}{\sum_{i=1}^r \omega_i \Delta C_{p,i@T_{g,i}}}$$

is written for binary mixtures as

$$T_{g,\text{mixture}} = \frac{\omega_1 \{\Delta C_{p,1@T_{g,1}}\} T_{g,1} + \omega_2 \{\Delta C_{p,2@T_{g,2}}\} T_{g,2}}{\omega_1 \Delta C_{p,1@T_{g,1}} + \omega_2 \Delta C_{p,2@T_{g,2}}}$$

which predicts that  $T_{g,\text{mixture}}$  lies between  $T_{g,1}$  and  $T_{g,2}$ . If one defines the ratio of specific heat discontinuities for both pure components at their respective glass transition temperatures as

$$\eta = \frac{\Delta C_{p,2@T_{g,2}}}{\Delta C_{p,1@T_{g,1}}}$$

then algebraic manipulation of the  $T_g$ -composition relation yields a linear form that is useful for actual data analysis:

$$T_{g,\text{mixture}} = T_{g,1} - \eta \frac{\omega_2}{\omega_1} \{T_{g,\text{mixture}} - T_{g,2}\}$$

Hence, one experimentally measures  $T_{g,\text{mixture}}$  versus  $\omega_2$ , where component 2 can be viewed as the plasticizer that depresses the glass transition temperature of the polymer. The first data pair at  $\omega_2 = 0$  is used to “force” the linear analysis described below to yield an intercept of  $T_{g,1}$ , which corresponds to the glass transition temperature of the

undiluted polymer. A first-order polynomial is required (i.e.,  $y = bx + c$ ) with dependent variable  $y = T_{g,\text{mixture}}$ , independent variable

$$x = \frac{\omega_2}{\omega_1} \{T_{g,\text{mixture}} - T_{g,2}\}$$

and slope  $b = -\eta$ . The pure-component data pair at  $\omega_2 = 1$  is excluded from the analysis. Linear least squares analysis is also possible if one employs the  $T_g$ –composition relation for binary mixtures that includes logarithmic temperatures instead of incorporating any of the approximations that yield the Gordon–Taylor equation. For example,

$$\begin{aligned} \ln(T_{g,\text{mixture}}) &= \frac{\sum_{i=1}^2 \omega_i \Delta C_{p,i@T_{g,i}} \ln(T_{g,i})}{\sum_{i=1}^2 \omega_i \Delta C_{p,i@T_{g,i}}} \\ &= \frac{\omega_1 \Delta C_{p,1@T_{g,1}} \ln(T_{g,1}) + \omega_2 \Delta C_{p,2@T_{g,2}} \ln(T_{g,2})}{\omega_1 \Delta C_{p,1@T_{g,1}} + \omega_2 \Delta C_{p,2@T_{g,2}}} \end{aligned}$$

where component 2 is viewed as the plasticizer. Rearrangement of the previous equation allows one to identify dependent and independent variables of a first-order polynomial for linear least squares analysis:

$$\ln(T_{g,\text{mixture}}) = \ln(T_{g,1}) - \eta \frac{\omega_2}{\omega_1} \left[ \ln \left( \frac{T_{g,\text{mixture}}}{T_{g,2}} \right) \right]$$

The appropriate polynomial model is  $y(x) = bx + c$ , and

- (i) the dependent variable is  $y = \ln(T_{g,\text{mixture}})$ ;
- (ii) the independent variable is  $x = \omega_2/\omega_1 \ln\{T_{g,\text{mixture}}/T_{g,2}\}$ ;
- (iii) the zeroth-order coefficient is forced to be  $c = \ln(T_{g,1})$ ;
- (iv) the first-order coefficient is  $b = -\eta$ .

The “fitting parameter”  $\eta$  should be interpreted as a ratio of discontinuous increments in specific heat for pure plasticizer relative to the undiluted polymer at their respective glass transition temperatures.

## 1.10 FREE VOLUME CONCEPTS

Qualitative and quantitative aspects of free volume are useful to analyze effects on  $T_g$  due to plasticizers, molecular weight, and pressure. Diffusion of solvents and gases in polymers occurs via the empty space between molecules that redistributes itself with little or no energy change. This empty space in a material results from the formation of holes or vacancies. The specific free volume associated with this empty space is

$$v_{\text{free}}(T) = v_{\text{actual}}(T) - v_{\text{occupied}}(T)$$

where  $v_{\text{actual}}$  represents the experimentally measured specific volume and  $v_{\text{occupied}}$ , defined by

$$v_{\text{occupied}}(T) = v_{\text{occupied}}(T = 0 \text{ K}) + v_{\text{free,interstitial}}(T)$$

represents the volume at absolute zero that is occupied by all of the atoms, as well as the space between the atoms known as interstitial free volume. Large amounts of energy are required to redistribute interstitial free volume and, hence, it is not very useful for molecular transport (i.e., diffusion of solvents and gases through polymers). In reference to the free space in a material that can be manipulated with relative ease, one defines fractional free volume as

$$f = \frac{v_{\text{free}}}{v_{\text{actual}}}$$

Manipulation of  $f$  can be achieved when one understands how fractional free volume depends on a variety of physicochemical parameters. Time-dependent effects on fractional free volume, such as densification and physical aging below the glass transition temperature, are not considered in the analyses below.

## 1.11 TEMPERATURE DEPENDENCE OF FRACTIONAL FREE VOLUME

The strategy is to expand the temperature dependence of actual and occupied specific volumes in a Taylor series about a reference temperature and truncate the nonlinear terms. The reference temperature is chosen as  $T_g$ . Above the glass transition temperature, actual volume expands according to  $\alpha_{\text{Liquid}}$ , whereas occupied volume expands according to  $\alpha_{\text{Glass}}$ . In other words,

$$\left\{ \frac{\partial \ln v_{\text{actual}}}{\partial T} \right\}_p = \alpha_{\text{Liquid}}$$

$$\left\{ \frac{\partial \ln v_{\text{occupied}}}{\partial T} \right\}_p = \alpha_{\text{Glass}}$$

At constant pressure, the polynomials that describe the temperature dependence of  $v_{\text{actual}}$  and  $v_{\text{occupied}}$  are

$$v_{\text{actual}}(T) = v_{\text{actual}}(T_g) + \left\{ \frac{\partial v_{\text{actual}}}{\partial T} \right\}_{p, T=T_g} (T - T_g) + \dots$$

$$v_{\text{occupied}}(T) = v_{\text{occupied}}(T_g) + \left\{ \frac{\partial v_{\text{occupied}}}{\partial T} \right\}_{p, T=T_g} (T - T_g) + \dots$$

These linear polynomials are written in terms of the appropriate coefficients of thermal expansion as follows:

$$v_{\text{actual}}(T) = v_{\text{actual}}(T_g) + (T - T_g)\alpha_{\text{Liquid}}v_{\text{actual}}(T = T_g) + \dots$$

$$v_{\text{occupied}}(T) = v_{\text{occupied}}(T_g) + (T - T_g)\alpha_{\text{Glass}}v_{\text{occupied}}(T = T_g) + \dots$$

By definition, the useful free volume is constructed by subtracting the previous two equations:

$$v_{\text{free}}(T) \approx \{v_{\text{actual}}(T_g) - v_{\text{occupied}}(T_g)\} + (T - T_g)\{\alpha_{\text{Liquid}}v_{\text{actual},T=T_g} - \alpha_{\text{Glass}}v_{\text{occupied},T=T_g}\}$$

This linear function for  $v_{\text{free}}(T)$  is divided by  $v_{\text{actual}}(T_g)$  to generate an approximate expression for fractional free volume. Hence,

$$f(T) \approx \frac{v_{\text{free}}(T)}{v_{\text{actual}}(T_g)}$$

Since  $v_{\text{free}}(T)$  is a linear function of temperature, and  $v_{\text{actual}}(T_g)$  is a zeroth-order function of temperature (i.e., a constant), the previous equation for fractional free volume should be linear in  $T$ . The result is

$$f(T) \approx \left\{ \frac{v_{\text{actual}}(T_g) - v_{\text{occupied}}(T_g)}{v_{\text{actual}}(T_g)} \right\} + \left\{ \frac{\alpha_{\text{Liquid}}v_{\text{actual}}(T_g) - \alpha_{\text{Glass}}v_{\text{occupied}}(T_g)}{v_{\text{actual}}(T_g)} \right\} (T - T_g) + \dots$$

The first term for  $f(T)$  on the right side of the previous equation is, by definition, the fractional free volume at the glass transition temperature,  $f(T_g)$ . The coefficient of  $\alpha_{\text{Glass}}$  in large brackets  $\{ \}$  in the second term on the right side of  $f(T)$  is the ratio of occupied to actual specific volumes at  $T_g$ , which is equivalent to

$$\frac{v_{\text{occupied}}(T_g)}{v_{\text{actual}}(T_g)} = \frac{v_{\text{actual}}(T_g) - v_{\text{free}}(T_g)}{v_{\text{actual}}(T_g)} = 1 - f(T_g)$$

Hence,

$$f(T) \approx f(T_g) + \{\alpha_{\text{Liquid}} - [1 - f(T_g)]\alpha_{\text{Glass}}\}(T - T_g) + \dots \\ \approx f(T_g) + \Delta\alpha(T - T_g) + \dots$$

where  $\Delta\alpha = \alpha_{\text{Liquid}} - \{1 - f(T_g)\}\alpha_{\text{Glass}}$ , which reduces to  $\alpha_{\text{Liquid}} - \alpha_{\text{Glass}}$  if the actual and occupied specific volumes are approximately equal at the glass transition temperature.

## 1.12 COMPOSITIONAL DEPENDENCE OF FRACTIONAL FREE VOLUME AND PLASTICIZER EFFICIENCY FOR BINARY MIXTURES

This analysis of the compositional dependence of fractional free volume is applicable to binary mixtures. When one of the components is a low-molecular-weight plasticizer, the dependence of fractional free volume on diluent volume fraction for trace amounts of diluent is identified as the plasticizer efficiency. In other words,

$$\lim_{\varphi_{\text{diluent}} \rightarrow 0} \left[ \left\{ \frac{\partial f_{\text{mixture}}}{\partial \varphi_{\text{diluent}}} \right\}_{T,p} \right] = \Gamma(T)$$

where  $\varphi_{\text{diluent}}$  is the volume fraction of the small molecule, and  $\Gamma(T)$  is the plasticizer efficiency parameter, or the difference between the pure-component fractional free volumes of diluent and polymer. This linear theory assumes that the actual volume and the useful free volume of a mixture of polymer and diluent can be obtained as a contribution from each pure component, with no change in actual volume or free volume upon mixing. This assumption might not be justified if small molecules occupy the empty space between chain molecules that originates from packing imperfections. In terms of extensive properties (i.e., volume) of individual components upon mixing,

$$\begin{aligned} V_{\text{actual,mixture}} &= V_{\text{actual,polymer}} + V_{\text{actual,diluent}} \\ V_{\text{free,mixture}} &= V_{\text{free,polymer}} + V_{\text{free,diluent}} \end{aligned}$$

then, by definition, the fractional free volume of the mixture is

$$\begin{aligned} f_{\text{mixture}} &= \frac{V_{\text{free,polymer}} + V_{\text{free,diluent}}}{V_{\text{actual,polymer}} + V_{\text{actual,diluent}}} \\ &= \left( \frac{V_{\text{free,polymer}}}{V_{\text{actual,polymer}}} \right) \varphi_{\text{polymer}} + \left( \frac{V_{\text{free,diluent}}}{V_{\text{actual,diluent}}} \right) \varphi_{\text{diluent}} \end{aligned}$$

where the volume fraction of component  $i$  is defined, in general, for a mixture of  $N$  components as

$$\varphi_i = \frac{V_{\text{actual,component } i}}{\sum_{j=1}^N V_{\text{actual,component } j}} = \frac{V_{\text{actual,component } i}}{V_{\text{actual,mixture}}}$$

The previous expression for  $f_{\text{mixture}}$  is simply a linear volume-fraction-weighted sum of the fractional free volume for each pure component in the mixture. Since all volume fractions must sum to unity, and the pure-component fractional free volume is defined by

$$f_{\text{component } i} = \frac{V_{\text{free,component } i}}{V_{\text{actual,component } i}}$$

the temperature and compositional dependence of a binary mixture's fractional free volume is

$$f_{\text{mixture}}(T, \varphi_{\text{diluent}}) = f_{\text{polymer}}(T) + \varphi_{\text{diluent}} \Gamma(T)$$

The plasticizer efficiency parameter is defined by

$$\Gamma(T) = f_{\text{diluent}}(T) - f_{\text{polymer}}(T)$$

From the previous section, the fractional free volume for each pure component is essentially a linear function of temperature. Hence,

$$\begin{aligned} \Gamma(T) &= \{ f_{\text{diluent}}(T_{\text{g,diluent}}) - f_{\text{polymer}}(T_{\text{g,polymer}}) \} \\ &\quad + \Delta\alpha_{\text{diluent}}(T - T_{\text{g,diluent}}) - \Delta\alpha_{\text{polymer}}(T - T_{\text{g,polymer}}) \end{aligned}$$

If (i) the glass transition is an “iso-free-volume” state such that any material exhibits about 2.5% useful empty space at its  $T_{\text{g}}$  when it is cooled from the molten

state at 5–10 °C/min, and (ii) the universal value for the discontinuous increment in thermal expansion coefficient at  $T_g$  is approximately  $4.8 \times 10^{-4} \text{ K}^{-1}$ , then the plasticizer efficiency parameter reduces to

$$\Gamma \approx 4.8 \times 10^{-4} \text{ K}^{-1} (T_{g,\text{polymer}} - T_{g,\text{diluent}})$$

Diluents with lower glass transition temperatures are better plasticizers for a given polymer. They induce larger reductions in  $T_g$  of the mixture because, at any temperature and diluent volume fraction, the fractional free volume of the mixture is larger when the plasticizer efficiency parameter increases. If the fractional free volume of a polymer–diluent mixture is larger, and presumably greater than 2.5%, then the material must experience a greater reduction in temperature to achieve the glassy state where  $f \approx 0.025$ . The concept of an “iso-free-volume” state at the glass transition temperature does not consider the rate dependence of  $T_g$  during heating or cooling traces that are required in actual experiments. A standardized cooling rate from the equilibrium viscous liquid state (i.e., 5–10 °C/min) is necessary to compare the effects of external factors on  $T_g$  via fractional free volume. The concept of plasticizer efficiency is useful if the primary objective is to decrease the glass transition temperature of an amorphous polymer. The only restriction is that polymer and diluent must be miscible so their mixture will yield a single  $T_g$ . Negative plasticizer efficiency implies that rigid aromatic-containing diluents with relatively high glass transition temperatures will increase a flexible polymer’s  $T_g$  when the diluent’s  $T_g$  is higher than that of the polymer. All theories of the compositional dependence of the glass transition temperature for mixtures predict that  $T_{g,\text{mixture}}$  is somewhere between the pure-component second-order phase transition temperatures. Thermal synergy is operative when  $T_{g,\text{mixture}}$  is higher than the glass transition temperature of each pure component. This is discussed in Chapter 6 when low-molecular-weight metal complexes from the d-block in the Periodic Table induce synergistic increases in the glass transition temperature of functional polymers that contain a lone pair of electrons on nitrogen in the side group. Exothermic energetic interactions are operative when transition-metal complexes coordinate to these functional sidegroups and increase  $T_g$ .

### 1.13 FRACTIONAL FREE VOLUME ANALYSIS OF MULTICOMPONENT MIXTURES: COMPOSITIONAL DEPENDENCE OF THE GLASS TRANSITION TEMPERATURE

Results from the previous section for binary polymer–diluent blends can be extended to mixtures of  $N$  components. The fractional free volume of the mixture is written as a linear volume-fraction-weighted sum of the fractional free volume for each pure component, neglecting any changes in actual and useful free volumes due to the mixing process. For example,

$$f_{\text{mixture}} = \sum_{i=1}^N \varphi_i f_{\text{component } i}$$

The temperature dependence of the fractional free volume of each pure component is

$$f_{\text{component } i}(T) \approx f_{\text{component } i}(T_{g,i}) + \Delta\alpha_i(T - T_{g,i}) + \dots$$

where the iso-free-volume assumption suggests that the leading term in the truncated series is approximately 0.025 for any material (i.e.,  $f_{\text{component } i}(T_{g,i}) \approx 0.025$ ). If  $f_{\text{mixture}}$  is evaluated at  $T_{g,\text{mixture}}$ , then the previous two equations yield

$$f_{\text{mixture}}(T = T_{g,\text{mixture}}) \approx 0.025$$

$$= \sum_{i=1}^N \varphi_i \{ f_{\text{component } i}(T_{g,i}) + \Delta\alpha_i(T_{g,\text{mixture}} - T_{g,i}) + \dots \}$$

Rearrangement yields the compositional dependence of the glass transition temperature of an  $N$ -component mixture via linear additivity of fractional free volume:

$$T_{g,\text{mixture}} = \frac{\sum_{i=1}^N \varphi_i T_{g,i} \Delta\alpha_{i,@T_{g,i}}}{\sum_{i=1}^N \varphi_i \Delta\alpha_{i,@T_{g,i}}}$$

The compositional dependence of  $T_g$  via volume continuity in Section 1.8 contains additional factors of pure-component specific volumes at  $T_{g,i}$  in each term of the numerator and denominator. The previous equation compares well with the Gordon–Taylor equation via entropy continuity:

$$T_{g,\text{mixture}} = \frac{\sum_{i=1}^N \omega_i T_{g,i} \Delta C_{pi,@T_{g,i}}}{\sum_{i=1}^N \omega_i \Delta C_{pi,@T_{g,i}}}$$

if volume fractions  $\varphi_i$  are replaced by mass fractions  $\omega_i$  and  $\Delta\alpha_i$  is replaced by  $\Delta C_{pi}$ .

## 1.14 MOLECULAR WEIGHT DEPENDENCE OF FRACTIONAL FREE VOLUME

There is a considerable amount of useful free volume in the vicinity of the chain ends due to packing imperfections. The concentration of chain ends, as determined by end-group titration, increases at lower molecular weights. The number-average molecular weight is most appropriate to account for the chain ends when polymers exhibit a broad distribution of molecular weights. In other words, it is better to use a mole-fraction-weighted average (i.e., the number-average molecular weight,  $M_n$ ) instead of a weight-fraction-weighted average (i.e., the weight-average molecular weight,  $M_w$ ) when all chains do not contain the same number of repeat units. One postulates the molecular weight dependence of fractional free volume to agree with these claims:

$$f(M_n) \approx f(M_n \Rightarrow \infty) + \frac{A}{M_n}$$

where the leading term on the right side of the previous equation represents the molecular-weight-insensitive fractional free volume for very high molecular weight polymers, and  $A$  is a positive constant on the order of 10–20 daltons for polymers that are produced via condensation mechanisms, and 200–500 daltons for polymers

that are produced via free radical mechanisms. If linear temperature dependence is included in the previous equation, then

$$\begin{aligned} f(T, M_n) &\approx f(T_g, M_n) + \Delta\alpha_{@T_g(M_n)} \{T - T_g(M_n)\} \\ &\approx f(T_g, M_n \Rightarrow \infty) + \Delta\alpha_{@T_g(M_n \Rightarrow \infty)} \{T - T_g(M_n \Rightarrow \infty)\} + \frac{A}{M_n} \end{aligned}$$

where the discontinuity in thermal expansion coefficient  $\Delta\alpha$  at the corresponding  $T_g$  is assumed to be independent of molecular weight. Since the glass transition is an iso-free-volume state, the leading terms,  $f(T_g, M_n)$  and  $f(T_g, M_n \Rightarrow \infty)$ , are approximately 0.025, and rearrangement yields the following expression for the molecular weight dependence of  $T_g$ :

$$T_g(M_n) \approx T_g(M_n \Rightarrow \infty) - \frac{A}{M_n \Delta\alpha}$$

$T_g(M_n \Rightarrow \infty)$  represents the molecular-weight-insensitive glass transition temperature that is tabulated in handbooks for many polymers. The previous equation suggests that  $T_g$  exhibits strong dependence on  $M_n$  at lower molecular weights, and approaches an asymptote when the concentration of chain ends diminishes significantly at very high molecular weights. The coefficient of the molecular-weight-sensitive term on the right side of the previous equation (i.e.,  $A/\Delta\alpha$ ) is on the order of (i)  $2-4 \times 10^4$  Da-K for condensation-type polymers and (ii)  $4-10 \times 10^5$  Da-K for free-radical-type polymers. In general, number-average molecular weights on the order of  $A/\Delta\alpha$ , with dimensions of daltons, are required to reach the molecular-weight-insensitive plateau on a graph of  $T_g$  versus  $M_n$ . When  $M_n$  approaches the magnitude of  $A/\Delta\alpha$ , there is at most a 1–2 degree difference between  $T_g(M_n \Rightarrow \infty)$  and the actual glass transition temperature, and this difference is below the detection limits of conventional calorimeters used to measure  $T_g$ .

## 1.15 EXPERIMENTAL DESIGN TO TEST THE MOLECULAR WEIGHT DEPENDENCE OF FRACTIONAL FREE VOLUME AND $T_g$

The following design strategy represents a logical sequence of experiments and analyses to quantify the information presented in the previous section.

1. Collaborate with a polymer chemist and synthesize several molecular weight fractions of an amorphous polymer. Molecular weight control and polydispersity are important considerations in the synthetic procedure.
2. Generate at least 10 different samples of the same polymer (i.e., polystyrene), where each sample contains chains with a different average number of repeat units. Hence, at least 10 different molecular weight fractions of the same polymer will be tested, as described below.
3. Each sample exhibits a distribution of chain lengths, which is analogous to a distribution of molecular weights. The first characterization technique

measures the molecular weight distribution of each sample, from which the number-average molecular weight is calculated. Hence, at least 10 different number-average molecular weights are calculated from the molecular weight distributions.

4. Gel permeation chromatography (GPC) is the separation technique that measures the molecular weight distribution of each sample. Larger chain molecules have smaller diffusion coefficients via the Stokes–Einstein equation, and they experience difficulty diffusing into the pores of the particles that are used to pack the chromatographic column. Hence, convective transport “sweeps” the larger chain molecules through the column before they have time to explore the internal structure of the packing via intrapellet diffusion. Consequently, larger chain molecules exit the column and contribute to the detector output curve before the smaller chain molecules. GPC is a separation technique based on the fact that molecules of different size have different residence times in the column. There is an inverse relation between molecular size and residence time, similar to the inverse relation between molecular size and intrapellet diffusion coefficients in porous catalytic pellets.
5. The GPC output curve for each sample reveals the distribution of chain lengths within each sample. This output curve is essentially the molecular weight distribution for the sample, from which the number-average molecular weight can be calculated via statistical analysis of the distribution.
6. Now that the number-average molecular weight of each sample is known, it is necessary to collaborate with a thermal analysis expert and obtain a differential scanning calorimetry (DSC) trace of each sample. These data correspond to specific heat versus temperature. If each sample is heated from the glassy state to the molten state, then one can calculate the glass transition temperature where the specific heat exhibits a discontinuity. More specifically,  $T_g$  is measured during the second or third heating trace and reported as the temperature where the discontinuity in  $C_p$  is approximately one-half of the total step increment in  $C_p$ . For example, one extends the *baseline heat capacity* of the glass into the molten state. A similar extrapolation of  $C_{p,\text{liquid}}$  below  $T_g$  is required so that both baseline heat capacities encompass a broad temperature range above and below  $T_g$ . Graphical evaluation of the glass transition temperature is obtained by (i) identifying two midpoints between the baseline heat capacities—one midpoint is above  $T_g$  and the other midpoint is below the phase transition; (ii) connecting these midpoints with a straight line; and (iii) locating the temperature where the straight line that connects the two midpoints intersects the actual calorimetric data. Now, at least 10  $M_n$ – $T_g$  data pairs are available.
7. Perform linear least squares analysis of the  $M_n$ – $T_g$  data pairs, realizing that the molecular weight dependence of the glass transition is

$$T_g(M_n) \approx T_g(M_n \Rightarrow \infty) - \frac{A}{M_n \Delta \alpha} \quad (1.5)$$

This model of  $T_g$  was obtained by postulating the molecular weight dependence of fractional free volume as follows:

$$f(M_n) \approx f(M_n \Rightarrow \infty) + \frac{A}{M_n} \quad (1.6)$$

where the molecular-weight-independent constant  $A$  is positive. Hence, linear least squares analysis of  $T_g$  versus  $1/M_n$  via a first-order polynomial should exhibit a negative slope because (i)  $A > 0$  and (ii) the discontinuity in thermal expansion coefficient at  $T_g$ ,  $\Delta\alpha = \alpha_{\text{Liquid}} - \alpha_{\text{Glass}}$ , is positive. The zeroth-order coefficient obtained from linear least squares analysis yields a good estimate of the molecular-weight-insensitive  $T_g$ , given by  $T_g(M_n \Rightarrow \infty)$  in Eq. (1.5).

8. Next, it is necessary to locate a dilatometer and measure the specific volume of each sample as a function of temperature from the glassy state to the highly viscous liquid state. The slope of  $\ln v_{\text{specific}}$  versus temperature corresponds to thermal expansion  $\alpha = (\partial \ln v_{\text{specific}} / \partial T)_p$ , which must be measured above and below  $T_g$  to calculate the discontinuity  $\Delta\alpha$  at the glass transition.
9. These two tests of the data should be self-consistent. If  $T_g$  versus  $1/M_n$  is *linear*, then the slope is constant and independent of molecular weight. Since the slope is  $-A/\Delta\alpha$ , the  $M_n - T_g$  data suggest that  $\Delta\alpha$  is not a function of molecular weight. This claim should be verified by calculating  $\Delta\alpha$  from dilatometry for each sample with a different number-average molecular weight.
10. If the discontinuity in thermal expansion is truly independent of molecular weight, then

$$A = \Delta\alpha_{@T_g} \left\{ -\frac{dT_g}{dM_n^{-1}} \right\}$$

Reasonable values for  $\Delta\alpha(@T_g)$  are on the order of  $5 \times 10^{-4} \text{ K}^{-1}$ , and typical ranges for  $A$  have been discussed previously for both free-radical and condensation polymers. Now, quantitative expressions are available for the molecular weight dependence of (i)  $T_g$  via Eq. (1.5) and (ii) fractional free volume via Eq. (1.6).

## 1.16 PRESSURE DEPENDENCE OF FRACTIONAL FREE VOLUME

Since the actual volume of a material decreases isothermally upon compression, one expects that the same is true for free volume. This is consistent with predictions from the Ehrenfest equations, which indicate that  $T_g$  increases at higher pressure. The strategy is to expand the pressure dependence of actual and occupied volumes in a Taylor series about a reference pressure, denoted by  $p_{\text{ref}}$ , and truncate the nonlinear terms. Above the glass transition temperature, actual volume compresses according to

$\beta_{\text{Liquid}}$ , whereas occupied volume compresses according to  $\beta_{\text{Glass}}$ . In other words

$$\left\{ \frac{\partial \ln v_{\text{actual}}}{\partial p} \right\}_T = -\beta_{\text{Liquid}}; \quad \left\{ \frac{\partial \ln v_{\text{occupied}}}{\partial p} \right\}_T = -\beta_{\text{Glass}}$$

At constant temperature, the polynomials that describe the pressure dependence of  $v_{\text{actual}}$  and  $v_{\text{occupied}}$  are

$$v_{\text{actual}}(p) \approx v_{\text{actual}}(p_{\text{ref}}) + \left\{ \frac{\partial v_{\text{actual}}}{\partial p} \right\}_{T=T_g} (p - p_{\text{ref}}) + \dots$$

$$v_{\text{occupied}}(p) \approx v_{\text{occupied}}(p_{\text{ref}}) + \left\{ \frac{\partial v_{\text{occupied}}}{\partial p} \right\}_{T=T_g} (p - p_{\text{ref}}) + \dots$$

These linear polynomials are written in terms of the appropriate coefficients of isothermal compressibility as follows:

$$v_{\text{actual}}(p) \approx v_{\text{actual}}(p_{\text{ref}}) - (p - p_{\text{ref}})\beta_{\text{Liquid}}v_{\text{actual}@p_{\text{ref}}} + \dots$$

$$v_{\text{occupied}}(p) \approx v_{\text{occupied}}(p_{\text{ref}}) - (p - p_{\text{ref}})\beta_{\text{Glass}}v_{\text{occupied}@p_{\text{ref}}} + \dots$$

By definition, the useful free volume is constructed by subtracting the previous two equations:

$$v_{\text{free}}(p) \approx \{v_{\text{actual}}(p_{\text{ref}}) - v_{\text{occupied}}(p_{\text{ref}})\} - (p - p_{\text{ref}})\{\beta_{\text{Liquid}}v_{\text{actual}@p_{\text{ref}}} - \beta_{\text{Glass}}v_{\text{occupied}@p_{\text{ref}}}\} + \dots$$

This linear function for  $v_{\text{free}}(p)$  is divided by  $v_{\text{actual}}(p_{\text{ref}})$  to generate an approximation for fractional free volume. Hence

$$f(p) \approx \frac{v_{\text{free}}(p)}{v_{\text{actual}@p_{\text{ref}}}}$$

Since  $v_{\text{free}}(p)$  is a linear function of temperature, and  $v_{\text{actual}}(p_{\text{ref}})$  is a zeroth-order function of temperature (i.e., a constant), the previous equation for fractional free volume should be linear in  $p$ . The result is

$$f(p) \approx \left\{ \frac{v_{\text{actual}}(p_{\text{ref}}) - v_{\text{occupied}}(p_{\text{ref}})}{v_{\text{actual}}(p_{\text{ref}})} \right\} - \left\{ \frac{\beta_{\text{Liquid}}v_{\text{actual}}(p_{\text{ref}}) - \beta_{\text{Glass}}v_{\text{occupied}}(p_{\text{ref}})}{v_{\text{actual}}(p_{\text{ref}})} \right\} (p - p_{\text{ref}}) + \dots$$

The first term for  $f(p)$  on the right side of the previous equation is, by definition, the fractional free volume at the reference pressure,  $f(p_{\text{ref}})$ . The coefficient of  $\beta_{\text{Glass}}$  in large brackets  $\{ \}$  in the second term on the right side of  $f(p)$  is the ratio of occupied to actual specific volumes at  $p_{\text{ref}}$ , which is equivalent to

$$\frac{v_{\text{occupied}}(p_{\text{ref}})}{v_{\text{actual}}(p_{\text{ref}})} = \frac{v_{\text{actual}}(p_{\text{ref}}) - v_{\text{free}}(p_{\text{ref}})}{v_{\text{actual}}(p_{\text{ref}})} = 1 - f(p_{\text{ref}})$$

Hence,

$$\begin{aligned} f(p) &\approx f(p_{\text{ref}}) - \{\beta_{\text{Liquid}} - [1 - f(p_{\text{ref}})]\beta_{\text{Glass}}\}(p - p_{\text{ref}}) + \dots \\ &\approx f(p_{\text{ref}}) - \Delta\beta(p - p_{\text{ref}}) + \dots \end{aligned}$$

where  $\Delta\beta = \beta_{\text{Liquid}} - \{1 - f(p_{\text{ref}})\}\beta_{\text{Glass}}$ , which reduces to  $\beta_{\text{Liquid}} - \beta_{\text{Glass}}$  if the actual and occupied specific volumes are approximately equal at  $p_{\text{ref}}$ .

## 1.17 EFFECT OF PARTICLE SIZE OR FILM THICKNESS ON THE GLASS TRANSITION TEMPERATURE

**Question:** Is  $T_g$  for a powder sample of a polymer the same as that for a thin film of the same polymer? How does particle size (i.e., for powders) or film thickness affect the glass transition temperature?

The 21 responses that follow were obtained from selected members of a discussion list that is maintained by the Division of Polymer Chemistry of the American Chemical Society. The responses have been edited for clarity and to ensure anonymity.

**RESPONSE #1:** The glass transition should not vary as a function of the physical state of the polymer. What might change is the ability to transfer heat adequately. For example, if one tests a thick sample via DSC, then there will be inefficient heat transfer between the bottom of the sample pan and the upper surface of the film. This is particularly important for most polymers that have low thermal conductivity. Consequently, the glass transition is broadened and shifted to higher temperatures, depending on the heating rate. Technically, all thermal transitions should not depend on particle size or film thickness.

**RESPONSE #2:** This is a debatable issue and a very interesting question. If glass transition temperatures are different for powders and films, then one should formulate a fundamental explanation of this phenomenon. Remember that  $T_g$  is typically a broad transition (maybe 10 °C) and the reported value depends on the experimental protocol, especially test frequency (i.e.,  $T_g$  is approximately 6 °C higher per decade increase in frequency) and midpoint-versus-onset measurement.

**RESPONSE #3:** The glass transition temperature depends on film thickness and molecular weight. As film thickness increases, it affects cure and powder properties.

**RESPONSE #4:** The difference between  $T_g$  values of powders and films depends on whether the powder is a thermosetting formulation (i.e., fusion-bonded epoxy) or a thermoplastic such as polyethylene or nylon. One measures a glass transition during the first heating trace that depends very much on thermal history, aging, stored mechanical energy from the powdering process, moisture content, plasticizing solvents, and so on. Annealing at temperatures just below  $T_g$  (i.e., enthalpy relaxation) will identify the “real” glass transition much more quickly than aging the sample for a few months at ambient temperature. Some of this information is available in the research literature on powder coatings. The work of Turi [1997] is described in definitive texts on this subject. An entire chapter is dedicated to the discussion of thin films.

**RESPONSE #5:** Glass transition temperature differences between powders, films, and fibers might be due to the fact that the amount of residual solvent is different in each sample.

Residual solvent content probably follows the following trend: film > powder > fiber, which will exert a plasticizing effect on the polymer and lower  $T_g$ . This trend is observed in the conversion of polyamic acids to polyimides, which is facilitated by residual solvent.

**RESPONSE #6:** This is a very active and controversial area of research, and universal trends have not been established. The lack of universality is related to different effects of the substrate and air interface on free volume and local packing of the chains. The effect of film thickness on the glass transition temperature should be important when the thickness is on the order of a few radii of gyration, at most.

**RESPONSE #7:**  $T_g$  decreases precipitously when film thicknesses are less than the dimensions of a single chain. This can be achieved by spin-coating ultrathin films onto substrates at sufficiently high rotational velocity such that centrifugal forces influence anisotropic chain conformations with larger projections of the segment vectors in the plane of the substrate.

**RESPONSE #8:** This research problem has not been resolved yet. In 1994, the glass transition temperature of polymer thin films was found to be different from that in the bulk for polystyrene spin-coated on silicon and PMMA on gold-coated silicon.  $T_g$  decreased by a maximum of 20% from the bulk value when film thickness was decreased. More recently, the same group of researchers investigated PMMA thin films on silicon and measured an increase in  $T_g$  as film thickness decreased. In the earlier work, interactions between the polymer and the substrate were weakly favorable, at most, whereas in the more recent study, PMMA–silicon interactions are strongly attractive. In other studies of the same phenomenon, random copolymers of styrene and methyl methacrylate form an interface between polystyrene homopolymer and the substrate for quantitative control of interfacial energy. Results suggest that the effect of film thickness on the glass transition temperature is not driven by interfacial energy considerations. Perturbations in local density of the polymer at the interface with the substrate are the most probable cause of different  $T_g$  values for bulk polymers and thin films, when film thickness is below approximately 500 Å. Similar effects for powdered samples of a given polymer are possible if particle size is below  $\sim 500$  Å with no aggregation among particles upon heating. The following references represent an introduction to the effects of particle size and film thickness on the glass transition temperature: Keddie et al. [1994a, b], Mayes [1994], Wallace et al. [1995], Forrest et al. [1996], Kajiyama et al. [1997], and Tsui et al. [2001].

**RESPONSE #9:** The glass transition temperature depends on molecular weight, crosslink density, comonomer composition, phase separation, degree of crystallinity, chemical structure, pressure, and the time scale of the measurements.  $T_g$  should be similar if the same polymer is studied as a film or a powder, and all of the above-mentioned parameters are constant.

**RESPONSE #10:** The glass transition temperature of a polymer depends on the heating rate employed. Film thickness affects the rate of heat transfer rate into the film. When films are produced from powders, the morphology of the polymer might change, which will influence  $T_g$ . For semicrystalline polymers, sample preparation procedures will change the size and perfection of the microcrystalline regions.

**RESPONSE #11:** The following points must be considered: (i) thin films yield more “definitive glass transition temperatures” than powdered samples of the same polymer; (ii) annealing below  $T_g$  will affect any subsequent measurements of the transition; (iii) thermal contact between the aluminum sample pan and the bottom of the sample is important; and (iv) thin films cast from solution might contain residual solvent that will plasticize the polymer.

**RESPONSE #12:** The glass transition temperature of a polymer is an inherent property of the material, but the actual value that one measures could depend on the experimental method used,

thermal history of the sample, and molecular weight. If powders and films of the same polymer have identical average molecular weight and polydispersity, then the second DSC heating trace after rapid thermal quenching should yield similar values that are independent of the sample's original physical state.

**RESPONSE #13:** If DSC is used to measure the glass transition temperature, then  $T_g$  might depend on the physical form of a polymer. Contact between the polymer and the bottom of the aluminum sample pan is required for heat transfer to increase the sample temperature. It is best to obtain several different measurements via DSC scans at a heating rate of  $2\text{ }^\circ\text{C}/\text{min}$  with approximately 7–10 milligrams of sample in a sealed environment. It might be difficult to observe a glass transition for powdered samples during the first heating trace. When thermoplastics are heated into the highly viscous liquid state above  $T_g$  and then cooled to lower temperatures, the physical state of the solid sample will change from a powder to a film, and this introduces unwanted complexity into the problem.

**RESPONSE #14:** The glass transition temperature depends on film thickness. There are indications from gas permeation measurements that very thin films on the order of 100 nm, or less, exhibit accelerated physical aging via volume and enthalpy relaxation, which yield higher  $T_g$  values than thicker films.

**RESPONSE #15:** The glass transition temperature should be the same for a fully amorphous sample of the same polymer. Since  $T_g$  depends on thermal and preparation history, different values of  $T_g$  will be measured for samples cast from solution versus cooling from the molten state. Thermal history can be erased by heating samples to temperatures above the highest thermal transition (i.e.,  $T_g$  or  $T_m$ ), but below the decomposition temperature. The degree of crystallization has an important role, and the rate of cooling must be considered. Rapid cooling or quenching will produce a glassy material, whereas slow cooling might allow some crystallization to occur. Hence, one expects to measure different glass transition temperatures during the second heating trace for powders, pellets, and films.

**RESPONSE #16:** Even though  $T_g$  is an intrinsic property of a material, it probably depends on film thickness or particle size because a discontinuous powder influences the rate of heat transfer through the aggregate differently than a solid film, thus affecting the rate at which the polymer experiences temperature changes.

**RESPONSE #17:** The answer depends on how the glass transition temperature is measured. If DSC experiments are performed, then when a powder reaches its  $T_g$ , it will fuse together and cause some thermal disturbance in the aluminum sample pan. Data are not reported from the first heating scan. On the second and subsequent heating scans, the sample is no longer in powder form. The effect of particle size or film thickness on  $T_g$  is observed when these dimensions are less than approximately  $0.1\text{ }\mu\text{m}$  (i.e., 100 nm).

**RESPONSE #18:** The glass transition temperature is a material constant and should not depend on sample thickness when it is measured using the correct tools, like precision calorimetry. Films might have different  $T_g$  values due to the effects of thermal history that can lead to different degrees of crystallinity.

**RESPONSE #19:** The glass transition temperature of a polymer depends on chemical structure and chain microstructure, but it is independent of the macroscopic form of the material (i.e., powder or thin film). If measurements nevertheless indicate differences, then the presence of contaminants, such as residual solvents in the case of cast films, might be the cause. Any species that is soluble in the polymer (plasticizer, surfactant, or other additives) should depress  $T_g$ .

**RESPONSE #20:** The physical state (i.e., powder or thin film) of any material should not affect the glass transition temperature. However, the measurement of  $T_g$  might reflect some dependence on size. Since  $T_g$  depends on heating or cooling rate, and the rate of heat transfer should be different for the different physical states, the apparent  $T_g$  might be different.

**RESPONSE #21:** The previous responses are fairly diverse and address very different questions. The powder question and questions related to history or method of measurement are only marginally related to the question of  $T_g$  in nanoscale structures. The latter is an area of active research. The problem in polymers should not be fundamentally different from the problem in small molecules if the glass transition event has “universal” features. Work on liquids confined to pores, or microemulsions, is very relevant to the question. The advantage of polymers is that stable films of nanometer thickness can be made. When this is done, supported films of polystyrene reveal modest  $T_g$  depression, similar to ortho-terphenyl in nanopores. Initial results on free-standing films describe rather large changes in  $T_g$ , and this transformed the paradigm from an interesting but not fully explained question to one of great interest because polymers are used routinely at temperatures that are more than 70%, and often greater than 90%, of their glass transition temperature. The problem of interest is: why do we see such a range of results? The glass transition temperature decreases, increases, remains the same, or even disappears, depending upon details of the experimental or molecular simulation conditions. Different behaviors have been observed for the same material subjected to different testing methods. In many cases, experiments have been performed carefully, and the results are reproducible. Existing theories of the glass transition cannot explain the range of behaviors seen at the nanometer scale, because the glass transition phenomenon is not fully understood. A mobile layer on the surface might explain some observations, but if there is a mobile layer that provides a complete explanation, then why does polystyrene show such large effects, whereas poly(methyl methacrylate) and poly(vinyl acetate) reveal a very small change, or no change, in  $T_g$  for the same free-standing film geometry? Furthermore, why do some systems, such as ortho-terphenyl and a few thermosetting polymers, reveal two glass transitions upon confinement in pores, where, in some cases, one  $T_g$  is higher than, and the other is lower than, the bulk  $T_g$ ? Or, why do polystyrene films on a glycerol surface exhibit no significant changes in  $T_g$ , as this geometry seems to be very similar to free-standing films? The question remains of considerable interest, currently there is no full explanation, and it may suggest that the “glass-is-a-glass” paradigm of the glass transition is not correct, as suggested by nanoscale measurements and results. *Courtesy of Greg McKenna, Department of Chemical Engineering, Texas Tech University, Lubbock, Texas, USA; November 2009.*

## 1.18 EFFECT OF THE GLASS TRANSITION ON SURFACE TENSION

**Question:** *How does the surface tension (or surface free energy) of polymers at an air interface vary with temperature as one passes through the glass transition?*

The responses that follow were obtained from selected members of a discussion list that is maintained by the Division of Polymer Chemistry of the American Chemical Society. The responses have been edited for clarity and to insure anonymity.

**RESPONSE #1:** Surface and interfacial energies have been measured by Wu [1970], who found that surface tension decreases at higher temperature, but there does not appear to be a significant discontinuity at the glass transition. The surface energy of glasses should be higher than that of rubber-like materials.

**RESPONSE #2:** Surface tension is described more appropriately as “surface equilibrium free energy.” Since glasses exist in a nonequilibrium state, surface tension is not well defined for these materials from the viewpoint of rigorous equilibrium thermodynamics. However, the temperature dependence of contact angle measurements should provide some useful insight (Neumann and Tanner [1970]). Kwok and Neumann [1999] review contact angle measurements and discuss various pitfalls. Della Volpe et al. (2006) discuss a method to obtain the equilibrium contact angle for water on poly(methylmethacrylate). Depending on the type of interface (i.e., polymer–air, polymer–water, polymer–solvent), surface tension exhibits time dependence as the polymer is exposed to the “other phase” until equilibrium is achieved. One expects that the surface tension dynamics of glassy polymers (i.e., the approach to equilibrium) is much weaker than that of rubbery polymers, due to reduced mobility below the glass transition temperature. Experimental problems will be encountered above  $T_g$  because surface tension measurements suffer from significant instabilities that are related directly to the high degree of mobility in the rubbery state. Since temperature changes have no effect on surface chemistry, thermal energy differences (i.e.,  $kT$ ) do not contribute much to the equilibrium surface free energy.

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**PROBLEMS**

- 1.1. Integrate both of the Ehrenfest equations and obtain explicit expressions for the pressure dependence of the glass transition temperature. Your answers should be cast in the following form:  $T_g = f(p)$ . In both cases, it is appropriate to assume that discontinuous observables at an equilibrium second-order phase transition are independent of temperature and pressure.

*Answer*

See the developments in Section 1.6.2, particularly Eqs. (1.3) and (1.4). The final results are

**Volume continuity**

$$T_g(p) \approx T_g(p_{\text{ref}}) + \frac{\Delta\beta_{@T_g}}{\Delta\alpha_{@T_g}}(p - p_{\text{ref}})$$

**Entropy continuity**

$$T_g(p) \approx T_g(p_{\text{ref}}) \exp\left\{\frac{(p - p_{\text{ref}})v_{@p_{\text{ref}}}\Delta\alpha_{@T_g}}{\Delta C_{p,@T_g}}\right\}$$

- 1.2. The following data are available for completely amorphous *atactic* polystyrene from various textbooks, the *Polymer Handbook*, and refereed journal literature:

Glass transition temperature at ambient pressure:  $T_g = 105^\circ\text{C}$

Density of the amorphous polymer:  $\rho_{\text{amorphous}} = 1.052\text{ g/cm}^3$

Coefficient of thermal expansion below the glass transition:  $\alpha_{\text{Glass}} = 1.9 \times 10^{-4}\text{ K}^{-1}$

Coefficient of thermal expansion above the glass transition:  $\alpha_{\text{Liquid}} = 5.6 \times 10^{-4}\text{ K}^{-1}$

Discontinuity in specific heat at the glass transition:  $\Delta C_p = 0.27\text{ J/(g}\cdot\text{K)}$

Universal gas constant:  $R_{\text{gas}} = 8.31\text{ J/g}\cdot\text{mol}\cdot\text{K} = 0.0823\text{ L}\cdot\text{atm}/(\text{g}\cdot\text{mol}\cdot\text{K})$

Begin with the statement of *entropy continuity* at  $T_g$  and calculate the equilibrium glass transition temperature of polystyrene subjected to an external pressure of 2500 atmospheres.

*Answer*

Use the second answer to Problem 1.1 and substitute numerical values for all of the thermophysical properties, as provided in the problem statement:

$$\begin{aligned} T_g(p = 2.5 \times 10^3 \text{ atm}) &= T_g(p_{\text{ref}}) \exp\left\{\frac{(p - p_{\text{ref}})v_{@p_{\text{ref}}}\Delta\alpha_{@T_g}}{\Delta C_{p,@T_g}}\right\} \\ &= [(105 + 273)\text{ K}] \exp\left\{\frac{(2499 \text{ atm}) \frac{1}{1.052 \text{ g/cm}^3} (5.6 - 1.9) 10^{-4} \text{ K}^{-1}}{0.27 \frac{\text{J}}{\text{g}\cdot\text{K}} \frac{82.3 (\text{cm}^3\cdot\text{atm})}{(\text{mol}\cdot\text{K})}}\right\} - 273 \text{ K} \\ &= 252^\circ\text{C} \end{aligned}$$

- 1.3. Estimate the magnitude of the discontinuity in the coefficient of isothermal compressibility,

$$\Delta\beta = \beta_{\text{Liquid}} - \beta_{\text{Glass}}; \quad \beta = -\left\{\frac{\partial \ln v}{\partial p}\right\}_T$$

for an amorphous polymer at its glass transition temperature. Express your answer in units of inverse atmospheres.

**Answer**

Use the differential form of the Ehrenfest equation, based on volume continuity in Section 1.6.1:

$$\frac{\partial T_g}{\partial p} = \frac{\Delta\beta_{@T_g}}{\Delta\alpha_{@T_g}} \approx 0.020 \text{ }^\circ\text{C/atm}$$

The universally accepted value for the pressure dependence of the glass transition temperature is that  $T_g$  increases by 20 K per  $10^3$  atmospheres, and the discontinuous increment in thermal expansion coefficients at  $T_g$  is  $\Delta\alpha \approx 4.8 \times 10^{-4} \text{ K}^{-1}$ . Hence,  $\Delta\beta$  at  $T_g$  is approximately  $10^{-5}$  inverse atmospheres, which corresponds to the coefficient of isothermal compressibility of viscous liquids, because glasses are extremely difficult to compress. For comparison, the coefficient of isothermal compressibility for ideal gases is  $1/p$ , approximately five or six orders-of-magnitude larger than that for liquids, which are typically assumed to be *incompressible*.

- 1.4. Sketch  $v\{r, T_g - 50 \text{ }^\circ\text{C}\} - v_{\text{equilibrium}}\{T_g - 50 \text{ }^\circ\text{C}\}$  versus the experimental cooling rate  $r$ , defined by  $r = -dT/dt$ , for an amorphous polymer that has been cooled from the equilibrium liquid state into the nonequilibrium glassy state at several different cooling rates. In other words, compare the difference between specific volume of the nonequilibrium and equilibrium glass, 50 °C below the glass transition temperature, as a function of the experimental cooling rate. *Is this a linear relation, or does the slope increase or decrease at high cooling rates?*
- 1.5. (a) Is it possible to invoke  $\Delta G = \Delta H - T_g \Delta S = 0$  at the glass transition temperature and rearrange this thermodynamic equation to calculate  $T_g$ ?

**Answer**

No, because enthalpy  $H$  and entropy  $S$  are continuous at second-order phase transitions, so rearrangement of  $\Delta G = 0$  yields an indeterminate ratio for  $T_g$ . The chemical potentials of the glass and viscous liquid are equivalent at the glass transition temperature, which yields  $\Delta G = 0$  at  $T_g$ . However, rearrangement of this equation does not provide useful information about the glass transition temperature, as it does at the melting temperature. In other words,  $T_m = \Delta H_{\text{fusion}}/\Delta S_{\text{fusion}}$  can be analyzed *qualitatively* to identify trends that affect the melting temperature (see Section 7.2.4).

- (b) Is it possible to invoke  $\Delta G = \Delta H - T_g \Delta S = 0$  at equilibrium second-order phase transitions, rearrange this thermodynamic equation, apply l'Hôpital's rule, and obtain an expression that allows one to analyze qualitative trends that affect the glass transition temperature? The extensive Gibbs free energy is denoted by  $G$ .

**Answer**

The answer is negative, regardless if one applies l'Hôpital's rule via differentiation of numerator and denominator, separately, with respect to temperature  $T$  or pressure  $p$ . In both cases, one obtains the identity  $T_g = T_g$ , which is correct, but not useful. Obviously, rearrangement of  $\Delta G = 0$  yields an indeterminate ratio for the glass transition temperature that can be analyzed further by invoking l'Hôpital's rule and differentiating numerator and denominator, separately, with respect to temperature at constant pressure:

$$T_g = \frac{\Delta H_{\text{Glass} \Rightarrow \text{Liquid}}}{\Delta S_{\text{Glass} \Rightarrow \text{Liquid}}} \xrightarrow{\lim_{T \rightarrow T_g}} \frac{\Delta \left\{ \frac{\partial H}{\partial T} \right\}_{p, \text{Glass} \Rightarrow \text{Liquid}}}{\Delta \left\{ \frac{\partial S}{\partial T} \right\}_{p, \text{Glass} \Rightarrow \text{Liquid}}} = \frac{\Delta C_{p, \text{Glass} \Rightarrow \text{Liquid}}}{\left\{ \frac{\Delta C_{p, \text{Glass} \Rightarrow \text{Liquid}}}{T_g} \right\}}$$

If one differentiates numerator and denominator, separately, with respect to pressure at constant temperature, then another trivial expression is obtained:

$$T_g = \frac{\Delta H_{\text{Glass} \Rightarrow \text{Liquid}}}{\Delta S_{\text{Glass} \Rightarrow \text{Liquid}}} \xrightarrow{\lim_{T \rightarrow T_g}} \frac{\Delta \left\{ \frac{\partial H}{\partial p} \right\}_{T, \text{Glass} \Rightarrow \text{Liquid}}}{\Delta \left\{ \frac{\partial S}{\partial p} \right\}_{T, \text{Glass} \Rightarrow \text{Liquid}}} \xrightarrow{\lim_{T \rightarrow T_g}} \frac{\Delta \left[ T \left\{ \frac{\partial S}{\partial p} \right\}_T + V \right]_{\text{Glass} \Rightarrow \text{Liquid}}}{-\Delta \left\{ \frac{\partial V}{\partial T} \right\}_{p, \text{Glass} \Rightarrow \text{Liquid}}}$$

$$\xrightarrow[\lim_{T \rightarrow T_g}]{\frac{\Delta T=0}{\Delta V=0}} \frac{T_g \Delta \left\{ \frac{\partial V}{\partial T} \right\}_{p, \text{Glass} \Rightarrow \text{Liquid}}}{\Delta \left\{ \frac{\partial V}{\partial T} \right\}_{p, \text{Glass} \Rightarrow \text{Liquid}}}$$

where  $dH = T dS + V dp$  and the Maxwell relation,  $\left\{ \frac{\partial S}{\partial p} \right\}_T = - \left\{ \frac{\partial V}{\partial T} \right\}_p$ , via the Gibbs free energy have been employed to implement l'Hôpital's rule via differentiation with respect to pressure.

- (c) Are the Gibbs free energies of the glass and the highly viscous liquid equivalent at the glass transition temperature?

**Answer**

Yes, if second-order phase transitions can be described by equilibrium thermodynamics. The Ehrenfest equations can be developed at the differential level by equating differential changes in the chemical potentials of the glass and viscous liquid on the transition line between these two phases. An indeterminate ratio is obtained for the pressure dependence of the glass transition temperature that can be analyzed further by invoking l'Hôpital's rule and differentiating numerator and denominator, separately, with respect to either temperature or pressure. It should be emphasized that the chemical potential of a pure material is synonymous with the molar Gibbs free energy.

- 1.6. (a) A miscible binary polymer–polymer blend exhibits a third-order thermodynamic phase transition at constant composition. Draw idealistic data from the heating trace in a

differential scanning calorimeter (i.e., heat capacity  $C_p$  vs. temperature) that allows one to identify this transition temperature.

**Answer**

Enthalpy versus temperature is discontinuous at first-order melting transitions, and idealistic heat capacities can be represented by delta functions. At second-order glass transitions, enthalpy versus temperature is continuous, but its temperature derivative (i.e.,  $C_p = \{\partial H/\partial T\}_p$ ), or heat capacity, versus temperature is discontinuous. At third-order thermodynamic phase transitions, heat capacity versus temperature is continuous, but its temperature derivative (i.e.,  $\{\partial C_p/\partial T\}_p$ ) versus temperature is discontinuous. Since DSC data are presented as  $C_p$  versus temperature, idealistic third-order phase transitions exhibit identical heat capacities for both phases, but there is a discontinuous increment in the slope of  $C_p$  versus temperature as materials are heated through the phase transition. It is impossible to identify third-order phase transitions via DSC because, under realistic conditions, the abrupt discontinuity in slope of  $C_p$  versus temperature is broadened such that positive curvature in the baseline cannot be distinguished from a phase transition of this nature.

- (b) *True or false:* The temperature dependence of specific enthalpy for a first-order phase transition is analogous to the temperature dependence of specific heat for a second-order phase transition.

**Answer**

True

- (c) *True or false:* The temperature dependence of specific enthalpy for a second-order phase transition is analogous to the temperature dependence of specific heat for a third-order phase transition.

**Answer**

True

- 1.7. Instead of invoking entropy continuity, the compositional dependence of the glass transition temperature of a miscible ternary polymer blend is developed by using the concept of *volume continuity* at  $T_{g,\text{mix}}$ . Without performing the tedious derivation, what is your best estimate of the final expression to calculate  $T_{g,\text{mix}}$ ?

**Answer**

The appropriate expression for the glass transition temperature of the ternary mixture is developed completely in Section 1.8. The final result is

$$T_{g,\text{mixture}} = \frac{\sum_{i=1}^3 \varphi_i T_{g,i} v_{i,@T_{g,i}} \Delta\alpha_{i,@T_{g,i}}}{\sum_{i=1}^3 \varphi_i v_{i,@T_{g,i}} \Delta\alpha_{i,@T_{g,i}}}$$

- 1.8. Identify seven assumptions that must be satisfied before one can invoke the Fox equation to describe the compositional dependence of ternary mixtures that contain two polymers and one UV stabilizer.

**Answer**

Use of the Fox equation for the compositional dependence of the glass transition temperature of binary or multicomponent mixtures requires that the following assumptions must be reasonable:

(i) Entropy continuity:

$$\begin{aligned} s_{i,\text{Liquid}}(T_{g,i}) &= s_{i,\text{Glass}}(T_{g,i}). \\ s_{\text{total,Liquid}}(T_{g,\text{mixture}}) &= s_{\text{total,Glass}}(T_{g,\text{mixture}}) \\ \Delta s_{\text{mixing,Liquid}}(T_{g,\text{mixture}}) &= \Delta s_{\text{mixing,Glass}}(T_{g,\text{mixture}}) \end{aligned}$$

(ii) Ideal mixtures:  $\omega_{i,\text{Glass}} = \omega_{i,\text{Liquid}}$ .

(iii) Upon heating,  $T_g$  occurs at constant pressure.

(iv) Temperature-independent specific heats:  $C_{pi,\text{Liquid}} \neq f(T)$ ,  $C_{pi,\text{Glass}} \neq f(T)$ .

(v) Expansion and truncation of  $\ln\{T_{g,i}/T_{g,k}\} \approx (T_{g,i}/T_{g,k}) - 1 + \dots$ .

(vi) The product  $T_{g,i}\Delta C_{pi}(@T_{g,i})$  must be the same for all pure components.

(vii) Homogeneous single-phase behavior is necessary.

1.9. (a) Consider homogeneous binary mixtures of a glassy polymer and a low-molecular-weight flexible plasticizer. The diluent concentration dependence of  $T_{g,\text{mixture}}$  is described by the Gordon–Taylor equation based on *linear additivity of fractional free volume*, as indicated below:

$$T_{g,\text{mixture}} = \frac{\varphi_{\text{Diluent}} T_{g,\text{Diluent}} \Delta\alpha_{\text{Diluent},@T_{g,\text{Diluent}}} + (1 - \varphi_{\text{Diluent}}) T_{g,\text{Polymer}} \Delta\alpha_{\text{Polymer},@T_{g,\text{Polymer}}}}{\varphi_{\text{Diluent}} \Delta\alpha_{\text{Diluent},@T_{g,\text{Diluent}}} + (1 - \varphi_{\text{Diluent}}) \Delta\alpha_{\text{Polymer},@T_{g,\text{Polymer}}}}$$

Obtain an expression for the initial slope of  $T_{g,\text{mixture}}$  versus plasticizer volume fraction  $\varphi_{\text{Diluent}}$ . In other words, calculate

$$\lim_{\varphi_{\text{Diluent}} \Rightarrow 0} \left\{ \frac{\partial T_{g,\text{mixture}}}{\partial \varphi_{\text{Diluent}}} \right\}_p$$

and simplify your answer as much as possible, such that it contains a total of four thermophysical properties in two terms (i.e., two thermophysical properties per component).

**Answer**

$$\lim_{\varphi_{\text{Diluent}} \Rightarrow 0} \left( \frac{\partial T_{g,\text{mixture}}}{\partial \varphi_{\text{Diluent}}} \right)_p = - \frac{\Delta\alpha_{\text{Diluent},@T_{g,\text{Diluent}}}}{\Delta\alpha_{\text{Polymer},@T_{g,\text{Polymer}}}} \{ T_{g,\text{Polymer}} - T_{g,\text{Diluent}} \}$$

(b) Is this initial slope from part (a) positive, negative, zero or too complex to determine? Identify any conditions that must be satisfied to support your answer.

**Answer**

The initial slope is *negative* if the glass transition temperature of the additive is less than that of the polymer and the binary mixtures do not exhibit phase separation, as they shouldn't in the limit of pure polymer. As pure materials are heated through their second-order phase transitions, they exhibit discontinuous increments in the coefficient of thermal expansion, so  $\Delta\alpha$  is greater than zero for polymer and diluent.

**1.10.** Dibutyl phthalate is a low-molecular-weight additive that functions as a plasticizer for polystyrene. The glass transition temperature of the pure polymer is  $105\text{ }^\circ\text{C}$ , and  $T_{g,\text{Diluent}}$  of the plasticizer is  $-91\text{ }^\circ\text{C}$ .

- (a) Estimate the glass transition temperature of plasticized polystyrene when the volume fraction of dibutyl phthalate is 20%. Volume fractions  $\varphi_i$  and mass fractions  $\omega_i$  are not significantly different when the densities of the two components are similar. A numerical answer is required here.

**Answer**

In the absence of thermophysical property data, like discontinuous increments in thermal expansion and specific heat at pure-component glass transition temperatures, use absolute temperature and apply the Fox equation:

$$\frac{1}{T_{g,\text{mixture}}} = \frac{\omega_{\text{Diluent}}}{T_{g,\text{Diluent}}} + \frac{1 - \omega_{\text{Diluent}}}{T_{g,\text{Polymer}}} = \frac{0.20}{(-91 + 273)\text{K}} + \frac{0.80}{(105 + 273)\text{K}}; \quad T_{g,\text{mixture}} \approx 38\text{ }^\circ\text{C}$$

- (b) Estimate the fractional free volume of the polymer–diluent blend at  $105\text{ }^\circ\text{C}$  when the volume fraction of plasticizer, dibutyl phthalate, is 20%.

**Answer**

The equations that are required to analyze this problem can be found in Sections 1.11 and 1.12. Temperature and compositional dependence of the binary mixture’s fractional free volume is

$$\begin{aligned} f_{\text{mixture}}(T = 105\text{ }^\circ\text{C}, \varphi_{\text{Diluent}} = 0.20) &\approx f_{\text{Polymer}}(T) + \varphi_{\text{Diluent}}\Gamma \approx 0.044 \\ f_{\text{Polymer}}(T) &\approx f_{\text{Polymer}}(T_{g,\text{Polymer}}) + \Delta\alpha_{\text{Polymer}@T_{g,\text{Polymer}}}(T - T_{g,\text{Polymer}}) \\ &= f_{\text{Polymer}}(T_{g,\text{Polymer}}) \approx 0.025 \\ \Gamma &\approx 4.8 \times 10^{-4}\text{ K}^{-1}(T_{g,\text{Polymer}} - T_{g,\text{Diluent}}) \approx 0.094 \end{aligned}$$

Note that the fractional free volume of the mixture at  $105\text{ }^\circ\text{C}$  (i.e., 4.4%) is greater than the universally accepted 2.5% empty space between molecules that all materials possess at their glass transition temperatures, because  $T = 105\text{ }^\circ\text{C}$  is greater than  $T_{g,\text{mixture}} \approx 38\text{ }^\circ\text{C}$ .

- (c) Does “volume relaxation” of the polymer–diluent blend via physical aging in the glassy state at ambient temperature (i.e.,  $20\text{ }^\circ\text{C}$ ) result primarily in a decrease in (1) the space between molecules (i.e., free volume available for molecular transport), or (2) the space between the atoms of each molecule (i.e., interstitial free volume)?

**Answer**

Densification, or physical aging in the glassy state, decreases the empty space between molecules that is available for molecular transport of gases and solvents through the glassy matrix.

- (d) Sketch  $T_{g,\text{mixture}}$  versus mass fraction of dibutyl phthalate  $\omega_{\text{Diluent}}$  in binary mixtures for the following five values of the “fitting parameter”  $\eta$ :

$$\eta = \Delta C_{p,\text{Diluent}}/\Delta C_{p,\text{Polymer}} = 0.25, 0.5, 1, 2, 4, 8$$

in the Gordon–Taylor equation. Put all five graphs on one set of axes and compare your predictions of  $T_{g,\text{mixture}}$  with those from the Fox equation.

**Answer**

The *additive rule of mixtures* (i.e., linear relation from  $T_{g,\text{Polymer}}$  at  $\omega_{\text{Diluent}} = 0$  to  $T_{g,\text{Diluent}}$  at  $\omega_{\text{Diluent}} = 1$ ) is obtained for  $T_{g,\text{mixture}}$  via the Gordon–Taylor equation when  $\eta = 1$ . Predictions for  $T_{g,\text{mixture}}$  lie (1) below the additive rule of mixtures when  $\eta > 1$ , and (2) above the additive rule of mixtures when  $0 < \eta < 1$ , as illustrated in Figure 1.1. The Fox equation exhibits weak nonlinear compositional dependence of the mixture’s glass transition temperature, such that  $T_{g,\text{mixture}}$  lies below the additive rule of mixtures and matches predictions for this binary mixture via the Gordon–Taylor equation when  $\eta = 2$ .

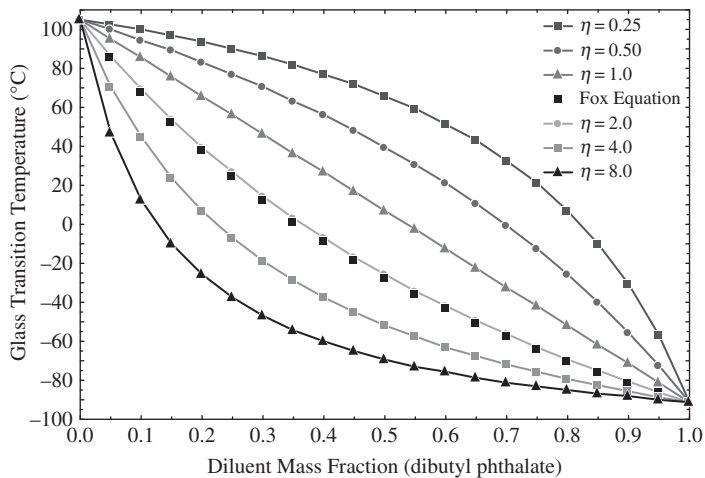
(e) Is it possible for a graph of

$$T_{g,\text{mixture}} \text{ versus } \frac{\omega_{\text{Diluent}}}{\omega_{\text{Polymer}}} \{T_{g,\text{mixture}} - T_{g,\text{Diluent}}\}$$

to exhibit a positive slope if the Gordon–Taylor equation adequately describes the compositional dependence of the glass transition temperature in miscible binary mixtures? The mass fraction of component  $i$  in the mixture is denoted by  $\omega_i$ .

**Answer**

No. These two quantities represent the dependent (i.e.,  $T_{g,\text{mixture}}$ ) and independent variables for linear least squares analysis of the Gordon–Taylor equation. Consult the discussion in



**Figure 1.1** Predictions from the Gordon–Taylor and Fox equations for the compositional dependence of the glass transition temperature of polystyrene in the presence of a miscible plasticizer, like dibutyl phthalate. The empirical fitting parameter  $\eta$  in the Gordon–Taylor equation is defined above in terms of the ratio of discontinuous increments in specific heats (i.e., diluent relative to polymer). The Fox equation only contains pure-component glass transition temperatures and mass fraction. Both equations are essentially identical when  $\eta = 2$ .

Section 1.9 for binary mixtures, and algebraically rearrange

$$T_{g,\text{mixture}} = \frac{\omega_{\text{Polymer}} \{ \Delta C_{p,\text{Polymer}@T_{g,\text{Polymer}}} \} T_{g,\text{Polymer}} + \omega_{\text{Diluent}} \{ \Delta C_{p,\text{Diluent}@T_{g,\text{Diluent}}} \} T_{g,\text{Diluent}}}{\omega_{\text{Polymer}} \Delta C_{p,\text{Polymer}@T_{g,\text{Polymer}}} + \omega_{\text{Diluent}} \Delta C_{p,\text{Diluent}@T_{g,\text{Diluent}}}}$$

to obtain the following linear form that is useful for actual data analysis:

$$T_{g,\text{mixture}} = T_{g,\text{Polymer}} - \frac{\Delta C_{p,\text{Diluent}@T_{g,\text{Diluent}}}}{\Delta C_{p,\text{Polymer}@T_{g,\text{Polymer}}}} \frac{\omega_{\text{Diluent}}}{\omega_{\text{Polymer}}} \{ T_{g,\text{mixture}} - T_{g,\text{Diluent}} \}$$

Hence, the slope of the graph under consideration is *negative* because it corresponds to the ratio of discontinuous increments in specific heat of the diluent relative to that of the polymer at their respective pure-component glass transition temperatures. Similar to thermal expansion and isothermal compressibility coefficients, there are no exceptions to the fact that specific heat exhibits a discontinuous increase as materials are heated through their glass transition temperatures. Hence, positive slopes are not allowed for the graph under consideration. However, if the Gordon–Taylor equation does not provide realistic predictions of  $T_{g,\text{mixture}}$  because diluents *increase* the glass transition temperature of the polymer, then positive slopes are possible but, now, the functional form of the compositional dependence of  $T_g$  should be reformulated.

**1.11.** Five possible plasticizers for polystyrene are under evaluation. The glass transition temperature of polystyrene is 105 °C, and  $\{ \Delta C_p \}_{\text{Polystyrene}}$  is 0.27 J/(g·K). The glass transition temperature of each plasticizer is approximately –95 °C. The discontinuous increment in specific heat for each additive at its pure-component glass transition temperature is summarized in Table 1.1.

- (a) Which diluent is most efficient in plasticizing polystyrene when the diluent mass fraction is 5%? In other words, which plasticizer induces the largest decrease in polystyrene’s  $T_g$  when all five polymer–diluent systems are compared at the same diluent mass fraction (i.e.,  $\omega_{\text{Diluent}} = 0.05$ )?

**Answer**

Plasticizer #4 is most efficient at decreasing the glass transition temperature of polystyrene, because  $\eta = \Delta C_{p,\text{Diluent}} / \Delta C_{p,\text{Polymer}}$  is largest for the five polymer–diluent combinations.

- (b) Provide support for your choice in part (a). *Hint:* Consider the answer to Problem 1.9a and Figure 1.1.

**Table 1.1** Representative Glass Transition Temperatures and Discontinuous Increments in Specific Heat for Five Small-Molecule Additives that Function as Plasticizers for Polystyrene

Diluent	$T_g$ (°C)	$\Delta C_{p,\text{Diluent}} @ T_g$ (J/(g·K))
Plasticizer #1	–95	0.35
Plasticizer #2	–95	0.20
Plasticizer #3	–95	0.30
Plasticizer #4	–95	0.40
Plasticizer #5	–95	0.30

**Answer**

Plasticizers with larger discontinuous increments in specific heat at their pure-component glass transition temperature,  $\Delta C_{p,\text{Diluent}@T_g}$ , exhibit larger *fitting parameters*  $\eta$  in the Gordon–Taylor equation for the compositional dependence of  $T_{g,\text{mixture}}$  in miscible blends with a given polymer. If the Gordon–Taylor equation yields adequate predictions of the glass transition temperature in these polymer–diluent blends, and all diluents have approximately the same pure-component glass transition temperature  $T_{g,\text{Diluent}}$ , then it should be obvious from Figure 1.1 that plasticizers with larger  $\Delta C_{p,\text{Diluent}@T_g}$  and larger  $\eta$  will be more efficient at decreasing the glass transition temperature of polystyrene when comparisons are made at the same diluent mass fraction. This conclusion is consistent with the fact that plasticizers with larger  $\Delta C_{p,\text{Diluent}@T_g}$ , but the same  $T_{g,\text{Diluent}}$ , induce steeper initial slopes of  $T_{g,\text{mixture}}$  versus  $\omega_{\text{Diluent}}$  in binary mixtures with the same polymer. The initial slope of the Gordon–Taylor equation, when analysis is based on *entropy continuity* instead of *linear additivity of fractional free volume*, can be obtained by analogy with the solution to problem 1.9a if one replaces (i)  $\Delta\alpha_i@T_{g,i}$  by  $\Delta C_{pi}@T_{g,i}$  and (ii) volume fraction  $\varphi_i$  by mass fraction  $\omega_i$ . The desired initial slope is

$$\lim_{\omega_{\text{Diluent}} \rightarrow 0} \left( \frac{\partial T_{g,\text{mixture}}}{\partial \omega_{\text{Diluent}}} \right)_p = - \frac{\Delta C_{p,\text{Diluent}@T_{g,\text{Diluent}}}}{\Delta C_{p,\text{Polymer}@T_{g,\text{Polymer}}}} \{ T_{g,\text{Polymer}} - T_{g,\text{Diluent}} \}$$

Hence, more efficient plasticizers with steeper initial slopes of  $T_{g,\text{mixture}}$  versus diluent concentration in miscible binary blends with the same polymer induce greater depression of the polymer's glass transition temperature.

- (c) Use only one set of axes and sketch the diluent concentration dependence of  $T_g$  for (i) polystyrene with plasticizer #1, and (ii) polystyrene with plasticizer #2. Put two curves on one set of axes.

**Answer**

These graphs of  $T_{g,\text{mixture}}$  versus plasticizer mass fraction are contained in Figure 1.1. The curve for plasticizer #1 lies *below* the additive rule of mixtures, because  $\eta > 1$ , and that for plasticizer #2 lies *above* the additive rule of mixtures, with  $\eta < 1$ . Plasticizer #1 is more efficient than plasticizer #2 at decreasing the glass transition temperature of polystyrene.

**1.12.** Experimental data are available for the compositional dependence of the glass transition temperature for single-phase homogeneous binary mixtures of polystyrene and dibutyl phthalate. This low-molecular-weight additive acts as a plasticizer and lowers the glass transition temperature of polystyrene at higher concentrations of dibutyl phthalate. The glass transition temperature of the plasticized polymer is described accurately by the Gordon–Taylor equation with fitting parameter  $\eta$ . This parameter represents the ratio of discontinuous increments in specific heat for the pure components, dibutyl phthalate relative to the polymer, at their respective pure-component glass transition temperatures, which are 105 °C for polystyrene and –91 °C for dibutyl phthalate.

- (a) Describe a data manipulation procedure based on *linear least-squares analysis* (LLSA) to calculate the fitting parameter  $\eta$ .
- (b) Estimate the fractional free volume of the polymer–diluent blend at 105 °C when the volume fraction of plasticizer, dibutyl phthalate, is 5%.
- (c) Estimate the glass transition temperature of plasticized polystyrene when the volume fraction of dibutyl phthalate is 5%. Volume fractions and weight fractions are not very different when the densities of the two components are similar.

- (d) Polystyrene and poly(phenylene oxide) represent a classic example of two high-molecular-weight polymers that form miscible binary mixtures in the solid state with a single composition-dependent glass transition temperature. Write an expression based on the Gordon–Taylor equation to estimate  $T_{g,\text{mixture}}$  for miscible ternary mixtures of polystyrene (PS) and poly(phenylene oxide) (PPO) that are plasticized by dibutyl phthalate (DBP).

**Answer**

The generalized Gordon–Taylor equation, based on entropy continuity at the glass transition, can be written explicitly for miscible ternary mixtures as follows:

$$T_{g,\text{mixture}} = \frac{\omega_{\text{PS}} \{ \Delta C_{p,\text{PS}@T_{g,\text{PS}}} \} T_{g,\text{PS}} + \omega_{\text{PPO}} \{ \Delta C_{p,\text{PPO}@T_{g,\text{PPO}}} \} T_{g,\text{PPO}} + \omega_{\text{DBP}} \{ \Delta C_{p,\text{DBP}@T_{g,\text{DBP}}} \} T_{g,\text{DBP}}}{\omega_{\text{PS}} \Delta C_{p,\text{PS}@T_{g,\text{PS}}} + \omega_{\text{PPO}} \Delta C_{p,\text{PPO}@T_{g,\text{PPO}}} + \omega_{\text{DBP}} \Delta C_{p,\text{DBP}@T_{g,\text{DBP}}}}$$

- 1.13.** The glass transition temperatures in Table 1.2 have been measured for four different molecular weight (i.e.,  $M_n$ ) fractions of a polymer that could be used as an oxygen barrier in food packaging applications.

When the sample with number-average molecular weight  $M_n = 2 \times 10^4$  Daltons was tested for oxygen permeability at ambient temperature, it was suggested that 50% reduction in its fractional free volume could achieve the desired oxygen barrier in the packaging material. *Qualitatively* describe the methodology to determine the lowest number-average molecular weight of this polymer that meets the desired specification at 25 °C. You should summarize a logical sequence of at least four steps to solve this problem.

**Answer**

$$M_n = 1.45 \times 10^5 \text{ Daltons}, T_g = 19 \text{ }^\circ\text{C}$$

- Step 1:** Linear least squares analysis of  $T_g(\text{K})$  versus  $1/M_n$  via a first-order polynomial yields a slope of  $-A/\Delta\alpha = -1.45 \times 10^6 \text{ K-Daltons}$ .
- Step 2:** The free volume parameter  $A$  is calculated from Step (1) via multiplication of  $-dT_g/d(1/M_n)$  by the universal value for the discontinuity in thermal expansion coefficient (i.e.,  $\Delta\alpha \approx 4.8 \times 10^{-4} \text{ K}^{-1}$ ). Hence,  $A = 696 \text{ Daltons}$ .

**Table 1.2** Representative Glass Transition Temperatures and Fractional Free Volume at 25 °C for Four Different Molecular Weight Fractions of an Amorphous Polymer

$M_n$ (Daltons)	$T_g$ (°C)	Fractional free volume at 25 °C
$2 \times 10^4$	-44	0.060 (i.e., 6%)
$5 \times 10^4$	0	
$2 \times 10^5$	+22	
$5 \times 10^5$	+26	

**Step 3:** When  $M_n = 2 \times 10^4$  Daltons,  $f = 0.060 = f(M_n \Rightarrow \infty) + A/M_n$ , allows one to calculate the ambient-temperature fractional free volume at very high molecular weight (i.e.,  $f(M_n \Rightarrow \infty)$ ).

**Step 4:** A 50% reduction in fractional free volume at 25 °C, based on the sample with  $M_n = 2 \times 10^4$  Daltons yields  $f = 0.030 = f(M_n \Rightarrow \infty) + A/M_n$ , which allows one to estimate the minimum molecular weight of this polymer that could be useful for packaging applications.

**1.14.** The following molecular weight dependence of fractional free volume for an amorphous polymer is postulated to agree with the fact that there is more empty space between polymer chains at lower molecular weight:

$$f(MW) \approx f(MW \Rightarrow \infty) + \frac{B}{MW^a}$$

where the exponent  $a$  is positive, and  $B$  is a constant on the order of (500 Daltons) <sup>$a$</sup> .

(a) Use this model for the molecular weight dependence of fractional free volume and predict the molecular weight dependence of  $T_g$ .

**Answer**

Express fractional free volume as a linear function of temperature, expanded about the molecular-weight-dependent glass transition temperature:

$$f\{T_g(MW)\} + \Delta\alpha\{T - T_g(MW)\} \approx f\{T_g(MW \Rightarrow \infty)\} + \Delta\alpha\{T - T_g(MW \Rightarrow \infty)\} + \frac{B}{MW^a}$$

Neglect any dependence of the discontinuity in thermal expansion coefficients on molecular weight and rearrange the previous equation, subjected to the approximation that the glass transition is an iso-free-volume state. Hence, the first terms on each side of the previous equation cancel. It might be necessary to measure specific volume versus temperature above and below  $T_g$  in a dilatometer for samples of the same polymer that have different number-average molecular weights. Then, the discontinuity in  $(\partial \ln v_{\text{specific}}/\partial T)_p$  at  $T_g$  can be calculated for each sample to verify or disprove the approximation that  $\Delta\alpha$  is molecular-weight independent. If all of the approximations mentioned above are valid, then

$$T_g(MW) \approx T_g(MW \Rightarrow \infty) - \frac{B}{(\Delta\alpha)MW^a}$$

which should be compared with similar predictions in Sections 1.14 and 1.15.

(b) Since  $T_g(MW \Rightarrow \infty)$  is tabulated in handbooks and textbooks, rearrange your  $T_g$  versus  $MW$  expression from part (a) and explain how linear least squares analysis can be implemented to calculate the exponent  $a$  from experimental data similar to those in Table 1.2.

**Answer**

Rearrange the previous equation for the molecular weight dependence of the glass transition temperature and take the logarithm of both sides. Be sure that the argument of each logarithm

is greater than zero.

$$\log[T_g(MW \Rightarrow \infty) - T_g(MW)] \approx \log\left(\frac{B}{\Delta\alpha}\right) - a \log(MW)$$

- (i) Polynomial model is  $y(x) = a_0 + a_1x$ .
  - (ii) Independent variable  $x$  is  $\log(MW)$ .
  - (iii) Dependent variable  $y$  is  $\log[T_g(MW \Rightarrow \infty) - T_g(MW)]$ .
  - (iv) The first-order coefficient, or slope, of the polynomial is  $a_1 = -a$ .
- (c) Sketch  $T_g$  versus  $MW$  when  $a = 1, 2,$  and  $3$ . Put all three curves on one set of axes.

**Answer**

When the exponent  $a$  is larger, molecular weight has a smaller effect on decreasing the glass transition temperature of the polymer. Furthermore, one achieves the molecular-weight-insensitive asymptotic limiting value of  $T_g$  at lower molecular weights when the exponent  $a$  is larger.

- 1.15.** Consider the following experimental description for completely amorphous polystyrene and then sketch (i) the dilatometer trace and (ii) the DSC trace for this material during the heating and subsequent cooling cycle. Be as quantitative as possible on the temperature axis.

“High molecular weight atactic polystyrene is subjected to 2500 atm pressure in the molten state at 300 °C. The high-pressure material is cooled rapidly to ambient temperature at 2500 atmospheres. Some of the material is placed in a dilatometer, and another piece of the same sample is tested in a differential scanning calorimeter. In both experiments, the polystyrene sample is heated at a rate of 10 °C/min to 300 °C and immediately cooled from 300 °C to ambient at the same rate.”

- (a) Sketch the temperature dependence of the data that are generated from the dilatometer.
- (b) Sketch the temperature dependence of the data that are generated from the differential scanning calorimeter.

