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Free Volume Theory and the Glass Transition

1. Specific Volume and Thermal Expansion

At high temperature, polymer segments can change their conformation rapidly. This dynamic equilibrium minimizes the overall potential energy of the system and results in a well-defined value of the specific volume $V(T)$ at a given temperature T. The temperature dependence arises from two main contributions:

- **anharmonicity of the intermolecular potential**: as vibrations grow with thermal energy, the average distance between neighboring segments increases.
- **conformational and translational mobility:** thermal energy allows chain segments to rearrange in space, further influencing the occupied volume.

As temperature decreases, $V(T)$ decreases. As long as the segments remain mobile (i.e. they can still explore conformations freely), the slope of $V(T)$ is constant and defines the **liquid-state thermal expansion coefficient:**

$$\alpha_{\text{liquid}} = \frac{1}{v_o}\frac{dV(T)}{dT}\bigg|_{\text{liquid}} , \tag{1}$$

where v_o is the volume the system would occupy in the absence of thermal vibrations (an extrapolated state at 0 K). Experimentally, α_{liquid} is nearly constant above the glass transition.

If equilibrium could be maintained down to very low temperatures, the system's specific volume would decrease linearly with temperature. As volume decreases, however, molecular motion becomes increasingly difficult. The limiting temperature at which conformational and translational motions would vanish defines the hypothetical "**thermodynamic" glass transition temperature T_0**. This state could only be reached under infinitely slow cooling, which is not realizable in practice.

2. Relaxation Times

In reality, cooling occurs at a finite rate $\Theta = \mathrm{d}T/\mathrm{d}t$. **To respond to a temperature change, the material requires molecular rearrangements characterized by a relaxation time τ, which is the average time for a segment to undergo a conformational change.** As volume decreases and free space becomes scarce, τ increases sharply.

When cooling from T_1 to T_2, the available time for conformational relaxation is

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$$\Delta t = \frac{T_1 - T_2}{\Theta} \quad . \tag{2}$$

If $\tau > \Delta t$, the system cannot equilibrate, and the **molecular conformations become frozen.** Below this point, the system still contracts due to reduced vibrations, but conformational motions no longer contribute. The slope of $V(T)$ decreases, defining the **glassy-state thermal expansion coefficient:**

$$\alpha_{\text{glass}} = \frac{1}{v_o}\frac{\mathrm{d}V(T)}{\mathrm{d}T}\bigg|_{\text{glass}} \quad . \tag{3}$$

The intersection of these two regimes (liquid vs. glass) provides **the experimental glass transition T_g.** Because T_g depends on the balance between τ and Δt, it varies with cooling or heating rate:

- faster cooling reduces Δt, the polymer has less time to relax, and T_g increases.
- slower cooling increases Δt, the polymer has more time to relax. T_g decreases.

Thus, T_g is not a fixed material constant but a kinetic quantity tied to the experimental timescale. **The physical state of the material in the glassy state therefore depends on the rate of cooling. The material is out of equilibrium at all temperatures below the measured T_g.** Only in the hypothetical limit of infinitely slow cooling would T_g converge to the "thermodynamic" glass transition temperature, T_0.

The specific volume in the equilibrated molten state can hence be written as

$$V(T) = \alpha_{\text{glass}} v_o T_o + \alpha_{\text{liquid}} v_o (T - T_o) \quad . \tag{4}$$

3. Free Volume

The **free volume theory** was first developed for simple liquids to explain why flow requires more space than is strictly occupied by the molecules themselves. In this view, not all of the material's volume is rigidly filled: small voids or "holes" exist that provide the necessary room for translational jumps and conformational rearrangements. These motions underlie relaxation, diffusion, and viscous flow.

At higher temperatures, thermal energy increases the number and size of such holes, thus enhancing mobility. As temperature decreases, the free volume shrinks, eventually arresting molecular motion.

The average free volume per segment, v_{fm}, can be defined as the excess volume of the liquid over the extrapolated glass at a given temperature, i.e. the additional volume present once the system is in the liquid state:

$$v_{\text{fm}} = \alpha_{\text{glass}} v_o T_o + \alpha_{\text{liquid}} v_o (T - T_o) - \alpha_{\text{glass}} v_o T = v_o (T - T_o)\Delta\alpha \quad , \tag{5}$$

where $\Delta\alpha = \alpha_{\text{liquid}} - \alpha_{\text{glass}}$. Graphically, this corresponds to the vertical distance between the liquid and glass lines in a plot of $V(T)$ versus temperature.

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At equilibrium, v_{fm} vanishes at $T = T_0$. For finite cooling rates, conformational relaxation stops at $T_g > T_0$. **A non-zero free volume is then trapped in the glassy state** (estimated to be about 2–3% of the total volume for amorphous polymers). The free volume directly controls relaxation times. A common expression is:

$$\tau = \tau_o \exp\left(\frac{v_o}{v_{\mathrm{fm}}}\right) \ , \tag{6}$$

where τ_o is a prefactor. It represents the minimal relaxation time of a segment if free volume were abundant, i.e. the intrinsic attempt time for a conformational jump (typically on the order of 10^{-12}–10^{-14} s, comparable to vibrational timescales of molecular bonds). The exponential factor v_o/v_{fm} expresses the likelihood of finding a hole large enough to accommodate a segmental displacement. For $v_{\mathrm{fm}} \gg v_o$, there is ample space and τ is minimal. When v_{fm} becomes comparable to or smaller than the segment size, such rearrangements become extremely rare, and relaxation times grow dramatically.

Viscous flow also depends on molecular rearrangements, and viscosity η is proportional to τ. Equation 6 thus resembles the empirical Doolittle relation for the viscosity of liquids:

$$\eta = \eta_o \exp\left(\frac{\mathrm{B}v_o}{v_{\mathrm{fm}}}\right) = \eta_o \exp\left(\frac{\mathrm{B}}{(T - T_o)\Delta\alpha}\right) \ . \tag{7}$$

where B is an empirical constant and η_o is a prefactor that can be thought of as the viscosity the liquid would have in the absence of steric hindrance to molecular rearrangements. This form suggests that as free volume shrinks (large v_o/v_{fm}), the viscosity increases drastically. The right-hand side obtained by substituting Equation 5 is formally identical to the empirical equation of Vogel, Fulcher, Tammann and Hesse (VFT or VFTH):

$$\eta = \eta_o \exp\left(\frac{\mathrm{A}}{T - T_o}\right) \ , \tag{8}$$

which is widely used to describe the viscosity of glass-forming liquids and polymers. It is mathematically equivalent to the well-known Williams–Landel–Ferry (WLF) equation, which we will discuss in more detail later in the course.

In this framework, the experimental T_g corresponds to the temperature where relaxation times exceed the experimental timescale. The thermodynamic T_0 is the hypothetical temperature where free volume vanishes and relaxation times diverge. In practice, fits to experimental data often place T_0 about 50 °C below the observed glass transition temperature, T_g.

4. Limitations

While the free volume model captures the dependence of viscosity and T_g on cooling rate, it simplifies reality. It treats the system as composed of identical, rigid units and neglects polymer-specific features such as chain connectivity and secondary interactions. In polymers, segmental motion persists above T_g, but the material becomes rubbery rather than liquid, with a shear modulus on the order of 1 MPa (three orders of magnitude lower than the glassy modulus).

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Nonetheless, the free volume theory provides a clear framework for linking specific volume, thermal expansion, relaxation times, and viscosity. It remains an invaluable tool for understanding the glass transition in polymers.

Additional Reading

R. P. White, J. E. G. Lipson. Polymer Free Volume and Its Connection to the Glass Transition. *Macromolecules* **2016**, *49*, 3987–4007.

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