

3.21 Kinetics of Materials—Spring 2006

March 22, 2006

Lecture 16: Diffusion in Noncrystalline Materials.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapter 10.

Key Concepts

- The kinetic theory of gases can be analyzed to yield an expression for the tracer self-diffusivity which will be proportional to $T^{3/2}$ and have an inverse dependence on pressure.
- A reasonable model for the structure of a simple liquid (e.g., monatomic) is the *dense random packed* hard-sphere model. Such structures possess a distribution of *free volume*. On a local scale the free volume in a liquid is in a constant state of change and the material behaves like a fluid.
- *Glasses* are essentially similar to liquids in that they possess a distribution of free volume but the structure is effectively “frozen-in” and the material behaves like a rigid solid. The change from liquid to glass occurs rather abruptly at the *glass transition temperature*.
- *Metallic glasses* can be produced from special alloy compositions by rapid cooling to avoid crystallization. Diffusion in metallic glasses has been extensively studied and differs in important ways from diffusion in metal crystals, indicating that self-diffusion must occur by a cooperative mechanism such as a ring mechanism, or more likely a chain-like motion of a group of atoms.
- Diffusion of small interstitial species in metallic glasses (e.g., hydrogen diffusion in Pd₈₀Si₂₀) is strongly dependent on the interstitial concentration. This finding is consistent with the fact that the metallic glass structure contains a distribution of interstitial sites with different free volume and consequently a distribution of energies when the sites are occupied by interstitials (see *KoM* Fig. 10.5).
- In *oxide glasses* such as SiO₂ the diffusivity of alkali species introduced as *network modifiers* increases with increasing concentration because such species break the random network of covalent bonds with bonds having more ionic character. At high modifier concentrations the modifier ions tend to cluster and form percolating channels that act as high-diffusivity paths in the structure.
- Long-chain polymer molecules in dilute solution adopt self-avoiding random walk conformations and diffuse by *Brownian motion*. D varies with molecular weight N as $N^{-1/2}$ or as $N^{-3/5}$ depending on the nature of the polymer–solvent interaction.
- Long-chain polymer melts have significant *entanglements* and diffuse by a *reptation* (“slithering”) process in which D varies as N^{-2} .

Related Exercises in *Kinetics of Materials*

None in Chapter 10!