611g Cluster Kinetics of Pressure-Induced Glass Formation

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Glass is a molecularly disordered, dense, and highly viscous form of matter formed when a fluid is cooled or compressed in a manner that avoids nucleation and crystallization. Widespread in nature and technology, glassy materials are ordinarily formed when organic or inorganic liquids are cooled sufficiently rapidly that nucleation cannot occur. Such materials are characterized by a huge increase in viscosity as temperature decreases. Although temperature effects for glassy materials have received more attention, the influence of pressure is also practically and theoretically important. Developing a quantitative understanding of glassforming transitions during supercooling or compression is a serious challenge in condensed matter science. The study of simple models is important to developing an understanding of glass. Our model presumes that fluctuations are cluster-based, dynamic restructuring processes in the metastable liquid or colloid. The model for fluctuations combines reversible growth and aggregation of solid clusters from monomer solute. As in previous work, we use distribution kinetics to formulate governing equations for reversible growth and aggregation processes for monomers and amorphous clusters. Clusters are groups of bonded molecules moving cooperatively; monomers in the fluid state are separately in random thermal motion. The resulting reactionlike equations represent fluctuating heterogeneous structures within the metastable liquid. Rate coefficients in these “reactions” are considered independent of cluster or monomer size, and all have temperature and pressure dependence given by transition-state theory. Population dynamics equations for the monomer and cluster can be formulated and solved for moments of the distributions, where zero moments are molar concentrations. Writing rate expressions directly according to the mass action principle, we find that growth and aggregation processes are second-order rate expressions in terms of concentrations, whereas dissociation and breakage are first-order. Localized thermodynamic equilibrium conditions are determined by setting time derivatives to zero in the rate equations, to obtain expressions for monomer and cluster concentrations in terms of rate coefficients. Transition-state expressions for the rate coefficients in terms of temperature and pressure provide activation energies and volumes. Utilizing free-volume theory to relate viscosity to the ratio of occupied to free volume, we propose an expression for viscosity in terms of the monomer and cluster concentrations, and therefore in terms of temperature, pressure, activation volume and activation energy. Since viscosity is proportional to dielectric relaxation time, the equation also relates dielectric relaxation time to temperature, pressure, activation volume and activation energy. The resulting equation contains two constants that are determined by known conditions of pressure and temperature. Two cases are examined: constant pressure and constant temperature. In the constant temperature case, all the activation energy terms cancel, leaving only the activation volume terms, as well as pressure and temperature. After some simplification, equations result that require only one parameter to fit viscosity or dielectric relaxation versus scaled temperature or pressure data. The constant temperature equation has been tested by fitting experimental data for eleven different compounds of widely varying molecular weights and different fragilities. Pressures above and significantly below the glass transition are included, and relaxation times vary over nearly five decades. Once the activation volume was determined for a compound at one temperature, it could successfully be used to predict dielectric relaxation time versus scaled pressure at another temperature. Constant pressure cases were also examined. After determining the activation volume at constant temperature for a compound, the activation energy was determined from a constant pressure experimental data set for that compound. Given both the activation volume and the activation energy for a compound, dielectric relaxation time versus scaled temperature could be predicted at a different pressure. The ability to predict dielectric relaxation at a second set of experimental conditions with parameters determined from data at other experimental conditions indicates that the activation volume and activation energy are independent of temperature and pressure. Two chemically similar compounds were also examined, and it was found that their activation volumes were roughly equivalent, as would be expected. The model allows for either a linear or a nonlinear relation of glass transition temperature to glass transition pressure, as found experimentally. By employing the van't Hoff equation that relates osmotic pressure to volume fraction of colloidal spheres, a relation can be obtained, based on the same distribution kinetics model, for viscosity in terms of volume fraction of particles in colloidal solutions, temperature, and an interparticle interaction fitting parameter. Viscosity is modeled as being proportional to the sum of colloid particle volume fraction and the interparticle attraction parameter divided by the temperature. There are two types of glass transitions seen in colloidal solutions, a repulsion-dominated glass and an attraction-dominated glass. The repulsion-dominated glass occurs at high volume fraction of colloidal particles. The attraction-dominated glass occurs as polymer is added to the system, causing interparticle attraction to increase. Thus the volume fraction term in the colloid viscosity model represents a density or entropic contribution to viscosity whereas the term containing the interparticle attraction parameter represents the energetic contribution to viscosity. It has been debated whether the glass transition is driven by temperature (energy) or by pressure/density (entropy). Our equation suggests that both contributions can be important. In summary, we have presented an interpretation of glass transition and metastable liquid or colloid behavior that includes both temperature and pressure influences. Rate equations for the cluster and monomer concentrations for the reactionlike processes lead to local equilibrium equations in terms of rate coefficients. Transition-state expressions for temperature and pressure effects provide activation energies and volumes. The free-volume theory shows how these rate expressions combine to yield a scaled equation for viscosity or dielectric relaxation. In the absence of nucleation, the amorphous phase transition behavior described by this kinetics approach appropriately correlates the temperature and pressure dependence of the glass transition and provides representations of metastable liquids or colloids exhibiting strong or fragile character.