

From Supercritical Fluids to Polymeric Glasses: A Unified Approach

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A series of experimental measurements are reported, which include phase equilibria, heats of mixing, volumetric properties, gas sorption, vibrational spectroscopy, and dielectric properties. The studied systems span the range from supercritical fluids to polymeric glasses. For the interpretation and correlation of the experimental data an equation-of-state framework is presented which can unify these seemingly diverse and uncorrelated phenomena. The model incorporates or can easily incorporate key concepts of modern molecular thermodynamics, such as molecular shape characteristics, non-randomness factors, hydrogen bonding, and order parameters. This capacity turns the model-framework applicable to vapors, liquids, liquid crystals, glasses, rubbers or gels, to homogeneous as well as to heterogeneous systems. An attempt is made to separate contributions from dispersion, dipolar, and hydrogen bonding interactions. Information sources, such as the solubility parameter data, are explored for this purpose. Interfacial profiles in hydrogen-bonded mixtures are discussed. New expressions for non-randomness are compared with literature expressions and with molecular simulation results.