

Defect Diffusion, Free Volume, Stretched Times and Divergent Time Scales Near the Glass Transition

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Employing an anomalous defect diffusion theory that was devised to explain stretched exponential relaxation and the accompanying Vogel type law, a new theory of free volume in glasses and glass-forming liquids is developed assuming a temperature/pressure dependent population of mobile single defects and immobile defects clusters. The defects encapsulate free volume and a defect cluster is found to possess less free volume than its separated constituent defect parts. The theory is applied to free volumes obtained from positron annihilation lifetime spectroscopy (PALS) studies of poly(propylene glycol) (PPG) 4000 over the wide temperature range from 15 K to 320 K and gives a good description of the free volume vs. temperature.