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"Energy Saturation as an Alternative Mechanism of the Glass Transition"

Abstract

A tangent hard sphere model in which each sphere interacts with nearby neighbors through a square well potential is solved in a quasi-chemical approximation. Attractive contributions to the configurational energy saturate well before reaching absolute zero temperature, a signature property of the new model. At saturation, a balance exists between repulsive and attractive forces that stabilize the liquid density, which thereafter becomes effectively independent of temperature. These low temperature, force stabilized states are identified as ideal glass states. Energy saturation at the glass temperature T_g appears to obtain in 23 of 25 polymers analyzed. This force balance at saturation raises the interesting question as to whether it defines a unique repulsive state. To address this question, electron density was used to measure the strength of repulsive forces; global electron densities were calculated at T_g and found to average 0.61 ± 0.03 mol/cc for 15 polymers that contain oxygen and 0.53 ± 0.02 mol/cc for 7 hydrocarbon polymers. Among 10 oxygen-containing polymers for which fragility indices have been measured, a good correlation between electron density and fragility was uncovered.