

Abstract Submitted
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Investigation of the Temperature-Dependent Specific Volume of Supported Polystyrene Films Upon Confinement XINRU HUANG, CONNIE ROTH, Dept. of Physics, Emory University — The experimentally observed large changes in the glass transition temperature T_g of ultrathin supported and free-standing polymer films with decreasing thickness h have puzzled the field for more than two decades. An open question at present is what material property changes correspond to the large shifts in film dynamics upon confinement. Thermodynamic theories have predicted that the observed $T_g(h)$ decrease in ultrathin polymer films may be tied to small shifts in the specific volume of the liquid-line above T_g . Here we use ellipsometry to investigate the temperature-dependent specific volume for supported polystyrene (PS) films of different thicknesses. Using the Lorentz-Lorenz parameter as a measure of the relative change in film density, we calculate the specific volume from temperature-dependent measurements of the index of refraction. While the slope of the liquid-line (thermal expansion coefficient) remains constant upon confinement, the $T_g(h)$ decrease is accompanied with a broadening of the transition and a small increase in the glassy-line thermal expansion, consistent with a larger fraction of the sample remaining liquid to lower temperatures. We find that both the liquid and glass specific volume lines shift together with decreasing thickness indicative of small 0.5-1% changes in overall film density with decreasing thickness.

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