

Temperature invariance of S_0 -parameter of polymers

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Abstract. The parameter S_0 which is characteristic of molten alkali halides and liquids has also been shown to be characteristic of a wide variety of polymers. Calculated data using the volume expansivity of the polymer establish the temperature invariance and constancy of the S_0 -parameter which retains, on an average, a constant value of 1.11 for polymers. Further understanding of the significance of fractional free volume and S_0 -parameter in describing various thermoacoustic properties and the anharmonic behaviour in polymers, has been developed.

Keywords. Polymer; S_0 -parameter; volume expansivity; heat capacity; Grüneisen parameter; fractional free volume.

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1. Introduction

The Grüneisen parameter has been shown to be an important quantity of current interest and useful as a measure of anharmonicity of molecular vibrations in studying the internal structure, molecular order and other thermoacoustic properties of polymers (Gibbons 1974; Sharma 1982a, b, 1983a, b). Recently Sharma (1983a) has shown that three dimensionless anharmonic parameters, the isobaric Γ , isochoric Γ'' and isothermal Γ' microscopic (lattice) Grüneisen parameters for polymers are related to each other. Following a model-dependent approximation by Dugdale and MacDonald (1953), which is valid at all pressures, Γ and Γ'' can be determined by using the isobaric and isochoric temperature dependence of bulk modulus respectively and Γ' from the isothermal pressure dependence of the bulk modulus for polymers (Sharma 1982a, b, 1983a, b). In this paper, an attempt has been made to relate Γ' (as a measure of anharmonicity of molecular vibration) with fractional free volume f (as a measure of disorder due to increased mobility of the molecules) and also the S_0 -parameter and evaluate them for a wide variety of polymers from the volume expansivity data at various temperatures. The S_0 -parameter which is characteristic of molten alkali halides, polyatomic ionic liquids, quasi-spherical molecular liquids and fluid hydrogen isotopes, has, on the average, a constant value of 1.11 ± 0.01 in a wide variety of substances (Sharma 1983d, 1985, 1986a, b). It is shown that the S_0 -parameter retains its constant

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