Thermoacoustical Parameters of Polymers at Low Temperatures

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SYNOPSIS

The Moelwyn-Hughes parameter has been utilized to evaluate a number of thermoacoustical parameters, viz., the Beyer nonlinear parameter; the isothermal, isobaric, and isochoric Grüneisen parameters; the repulsive exponent of intermolecular potential; the molecular constant; the fractional available volume; the Sharma thermoacoustical parameter S_0; and the Anderson–Grüneisen parameter for a wide variety of polymers at different low temperatures. A relationship among the isobaric, isothermal, and isochoric microscopic (lattice) Grüneisen parameters has been examined and analyzed in the case of several polymers. The results have been used to develop understanding of the significance of microscopic factors such as molecular order and intermolecular forces upon macroscopic thermoacoustic properties. The parameter S_0 remains invariant with temperature over a wide range and retains, on average, a constant value of 1.10 for several polymers at low temperatures, similar to a wide variety of substances. The present treatment has the distinct advantage that several thermoacoustic parameters can be evaluated from the knowledge of volume expansivity data alone. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The Grüneisen parameter, first introduced by Grüneisen,[1] is an important quantity of current interest that has been found very useful in studying the internal structure, molecular order, anharmonicity, and other thermoacoustic properties of liquids, liquefied gases, molten metals, solid polymers, etc.[2-17] This parameter, which is of fundamental significance in the equation-of-state calculations, serves as an effective guide in determining the mechanism of ultrasonic absorption in polymers and establishing a correlation with the results of phonon–phonon interaction absorption.[2] Warfield[4] pointed out that in polymers there are two distinct modes of lattice vibrations, viz., interchain (low frequency, long wavelength, and anharmonic) vibrations between the polymer chains involving weak van der Waals bonds and the intrachain (high frequency, short

wavelength, harmonic) vibrations along the polymer chain involving strong covalent bonds. By treating polymers as quasi-solids, the anharmonicity of postulated lattice vibrations has been shown to be exhibited only by the interchain vibrations.[5,6] Hence, calculations governed by these interchain vibrations determine the microscopic or lattice Grüneisen parameter Γ, whereas those dependent on all modes including both interchain and intrachain mode vibrations, on average, give the thermodynamic Grüneisen parameter $\bar{\Gamma}$ employing the thermodynamic parameters such as the heat capacity, thermal expansion, and thermal conductivity. These two types of Grüneisen parameters have been related to the ratio of interchain-to-intrachain mode vibrations in case of polymers[2,4,5,18] and also to polymer structure.[8] Interrelationships among the isothermal, isobaric, and isochoric Grüneisen and acoustical parameters have also been found.[9,19,20]

The Moelwyn-Hughes parameter[21] is of great importance because of its close relationship with the Grüneisen parameter[16] and some thermoacoustical parameters. It is one of the fundamental parameters used to evaluate thermoacoustical parameters in molten metals, liquefied gases, and polymers.[10,15]

In our earlier article,[14] we estimated a number of thermoacoustical parameters in polymers at low temperatures using the volume expansivity (α) data. In the present study, we estimate a few other thermoacoustic parameters, namely, the Moelwyn-Hughes parameter; the Beyer nonlinearity parameter; the Rao acoustical parameter; isothermal, isobaric, and isochoric Grüneisen parameters; the isothermal Anderson–Grüneisen parameter; the Sharma thermoacoustical parameter; the free available volume; the reduced bulk modulus; and the repulsive exponent of the intermolecular potential and molecular constant in several polymers at different low temperatures following the method suggested by Sharma and Reddy. The results are explained in the light of the temperature dependence of α.

THEORETICAL

Dugdale and MacDonald[21] obtained a more general expression for the microscopic or lattice Grüneisen parameter Γ, defined as a measure of the anharmonicity of normal mode frequency ν of lattice vibrations with molar volume V^1, which is valid at all pressures and provides a considerable improvement over that of Slater,[22] as given by Chang[23] as

$$\Gamma = -\left[\frac{\partial \ln \nu}{\partial \ln V}\right] = \left(-\frac{1}{2}\right) + \frac{1}{2}\left(\frac{\partial \ln \beta}{\partial \ln V}\right) \quad (1)$$

The thermodynamic (or average) Grüneisen parameter $\bar{\Gamma}$, which is governed by the molecular order and structure, is usually defined by the relation[2,4,16,24]

$$\bar{\Gamma} = \frac{\alpha V}{\beta C_V} = \frac{\alpha V}{\beta_s C_P} = \frac{\gamma - 1}{\alpha T} \quad (2)$$

Sharma[11,24] mentioned that, for metals, ionic crystals, and liquefied gases, $\Gamma \approx \bar{\Gamma}$, but for polymers, this is not true, and the ratio ($\Gamma/\bar{\Gamma}$) may vary from about 4 to 30.[2,4,18,25] Wada et al.[5] pointed out that since only the interchain vibrations contributed to Γ it is reasonable to consider the effect of interchain vibrations on both isobaric and isochoric heat capacites, heat capacity ratio, and the adiabatic compressibility. Equation (2) can be correspondingly modified to include contributions to both the heat capacities (C_P and C_V), β_s, and γ due to interchain vibrations as[4,16,18]

$$\Gamma = \frac{\alpha V}{\beta C_{V,i}} = \frac{\alpha V}{\beta_s C_{P,i}} = \frac{\gamma_i - 1}{\alpha T} \quad (3)$$

Equations (2) and (3) yield the following relation[24]:

$$Z = \left(\frac{C_{P,i}}{C_P}\right) = \left(\frac{C_{V,i}}{C_V}\right)\left(\frac{\gamma_i}{\gamma}\right) = XY \quad (4)$$

in which

$$X = \left(\frac{\bar{\Gamma}}{\Gamma}\right) = \left(\frac{C_{V,i}}{C_V}\right) = \frac{(\gamma - 1)}{(\gamma_i - 1)} \quad (5)$$

$$Y = \left(\frac{\beta_s}{\beta_{s,i}}\right) = \left(\frac{\gamma_i}{\gamma}\right) = \frac{(1 + \Gamma\alpha T)}{(1 + \bar{\Gamma}\alpha T)} \quad (6)$$

Equations (4)–(7) show that the quantities Z, Y, and X are of some interest, since these measure, respectively, the interchain contribution to C_P, C_V, γ, and β_s that interacts with the volume for polymers. Since the value of Y is expected to be unity,[24] the interchain contributions to C_P should be much higher by the factor Y than the contribution to C_V in polymers. This implies that the quantity Y is of some interest in the case of polymers, since it measures the ratio of that part of the interchain heat capacity ratio (and, hence, adiabatic compressibility), which interacts with volume. The quantity Y can also be expressed in the following forms[26]:

$$Y = [3(5\bar{V}^{1/3} - 2)]^{-1} \quad (7)$$

or

$$Y = \left[9 + \left(\frac{5\alpha T}{1 + \alpha T)}\right)\right]^{-1} \quad (8)$$

Moelwyn-Hughes[27] defined the C_1 parameter (dimensionless) as the pressure coefficient of the isothermal bulk modulus (the reciprocal of isothermal compressibility), which may be written in differential form as

$$C_1 = \left[\frac{\partial(1/\beta)}{\partial P}\right]_T = \left(\frac{1}{\beta}\right)\left[\frac{\partial \ln \beta}{\partial P}\right]_T = \left[\frac{\partial \ln \beta}{\partial \ln V}\right]_T \quad (9)$$

Treating polymers as quasi-solids, and using relevant expressions for the thermal expansion coefficient α and compressibility derived earlier,[28] it has been shown by Sharma[18] that the C_1 parameter can expressed in terms of α as

$$C_1 = \frac{13}{3} + (\alpha T)^{-1} + \frac{4}{3}(\alpha T) \quad (10)$$

Rao[19] defined an acoustical parameter K for liquids as the ratio of the temperature coefficient of the ultrasonic velocity U to the thermal expansion coefficient α. It has been pointed out[29] that K is about 3 for unassociated organic liquids near room temperature and 2 for liquefied gases and takes a rather scattered value for molten metals. However, the value of K depends on the type of intermolecular potential.[30] Yamamoto and Wada[29] showed that the value of K varies from polymer to polymer and K remains constant below and above the transition point for each polymer. Warfield and Hartmann[31] showed that the bulk modulus, Grüneisen constant, and Rao's constant have very strong temperature dependence. It has been shown[18,32] that Rao's constant K is closely related to the Moelwyn-Hughes parameter C_1 and to the isothermal Grüneisen parameter Γ_{ith} as

$$K = \Gamma_{ith} = \frac{C_1 - 1}{2} \qquad (11)$$

Equation (11) establishes the similarity of Γ_{ith} with K and its results are in good agreement with Warfield and Hartmann.[31]

Assuming to a first approximation the temperature independence of the Moelwyn-Hughes parameter C_1, it can be shown that[27]

$$\tilde{B} = [\tilde{V}^{C_1}]^{-1} \qquad (12)$$

The reduced volume $\tilde{V}$ can be expressed in terms of the zero-pressure limit as[11]

$$(\tilde{V}^{1/3} - 1) = \frac{\alpha T}{3(1 + \alpha T)} \qquad (13)$$

Assuming the ultrasonic velocity U as a function of both volume and temperature, the change in ultrasonic velocity can be written in the form[11]

$$\Delta U = \left(\frac{\partial U}{\partial T}\right)_V \Delta V + \left(\frac{\partial U}{\partial V}\right)_T \Delta V \qquad (14)$$

At constant pressure, eq. (14) may be rewritten as

$$\left(\frac{1}{U}\right)\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{1}{U}\right)\left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{1}{U}\right)\left(\frac{\partial U}{\partial P}\right)_T$$
$$\times \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad (15)$$

Using thermodynamic relations for α and β, it follows from eq. (15) that

$$\left(\frac{\partial \ln U}{\partial P}\right)_T = \left[\left(\frac{\partial \ln U}{\partial T}\right)_V - \left(\frac{\partial \ln U}{\partial T}\right)_P\right]\left(\frac{\beta}{\alpha}\right) \qquad (16)$$

Equation (16) yields a simple relation between the acoustical parameters as

$$K_{ith} = K_{iba} + K_{ich} \qquad (17)$$

in which

$$K_{ich} = K_{ith} - K_{iba} = \left(\frac{1}{\alpha}\right)\left(\frac{\partial \ln U}{\partial T}\right)_V$$
$$= \left(\frac{1}{\beta}\right)\left(\frac{\partial \ln U}{\partial P}\right)_T \qquad (18)$$

$$K_{iba} = -\left(\frac{\partial \ln U}{\partial \ln V}\right)_P = -\left(\frac{1}{\alpha}\right)\left(\frac{\partial \ln U}{\partial T}\right)_P \qquad (19)$$

$$K_{ith} = -\left(\frac{\partial \ln U}{\partial \ln V}\right)_T = \left(\frac{1}{\beta}\right)\left(\frac{\partial \ln U}{\partial P}\right)_T \qquad (20)$$

Following Grüneisen's assumption that all normal mode frequencies are equal, the change in normal mode frequency may be represented as[33]

$$\Delta \nu = \left(\frac{\partial \nu}{\partial T}\right)_V \Delta T + \left(\frac{\partial \nu}{\partial V}\right)_T \Delta V \qquad (21)$$

Sharma[9,33] introduced three dimensionless anharmonic parameters for the liquid state, namely, the isobaric (Γ_{iba}), isothermal (Γ_{ith}), and the isochoric (Γ_{ich}) microscopic Grüneisen parameters, which may be shown to be related as

$$\Gamma_{ith} = \Gamma_{iba} + \Gamma_{ich} \qquad (22)$$

where the Γ's are defined similar to the K's by replacing U with ν in eqs. (18)–(20) as

$$\Gamma_{iba} = -\left(\frac{\partial \ln \nu}{\partial \ln V}\right)_P = -\left(\frac{1}{\alpha}\right)\left(\frac{\partial \ln \nu}{\partial T}\right)_P \qquad (23)$$

$$\Gamma_{ith} = -\left(\frac{\partial \ln \nu}{\partial \ln V}\right)_T = \left(\frac{1}{\beta}\right)\left(\frac{\partial \ln \nu}{\partial P}\right)_T \qquad (24)$$

$$\Gamma_{ich} = \left(\frac{1}{\alpha T}\right)\left(\frac{\partial \ln \nu}{\partial \ln T}\right)_V = \left(\frac{1}{\beta}\right)\left(\frac{\partial \ln \nu}{\partial P}\right)_V \qquad (25)$$

Thus, the microscopic isobaric Γ_{iba}, isothermal Γ_{ith}, and isochoric Γ_{ich} Grüneisen parameters for the

polymers are essentially the same as the corresponding isobaric K_{iba}, isothermal K_{ith}, and isochoric K_{ich} acoustical parameters for liquids.

The isothermal Grüneisen parameter Γ_{ith} is evaluated from eq. (11) using the value of C_1. The isochoric Grüneisen parameter could be evaluated by using the following expression[4]:

$$\Gamma_{ich} = -(E - F)/F \qquad (26)$$

where $E = [2 + (\alpha T)^{-1}(-2\alpha)\, \check{V}^{\,C_1}]^{-1}$ and $F = -2\alpha$. Using the values of Γ_{ith} and Γ_{ich}, one can evaluate the isobaric Grüneisen parameter Γ_{iba} from eq. (22).

Assuming that the bulk modulus of a polymer depends only on volume,[2,16] the isobaric and isothermal Grüneisen parameters can be determined either by using temperature measurements or pressure measurements with the relations[2,4,16,17]

$$\left.\begin{aligned} \Gamma_{iba} &= -\left(\frac{1}{2\alpha}\right)\left(\frac{\partial \ln B_s}{\partial T}\right)_P \\[2mm] \text{and} \\[2mm] \Gamma_{ith} &= \left(\frac{1}{2}\right)\left(\frac{\partial B_s}{\partial P}\right)_T \end{aligned}\right\} \qquad (27)$$

The bulk sound speed can be expressed in terms of the bulk modulus as

$$U = (B_s/\rho)^{1/2} \qquad (28)$$

Using eq. (28) in eqs. (19) and (27), we obtain

$$\delta = 2K_{iba} + 1 = 2\Gamma_{iba} \qquad (29)$$

where δ is the isothermal Anderson–Grüneisen parameter given by[34,35]

$$\delta = -\left(\frac{1}{\alpha}\right)\left(\frac{\partial \ln B_s}{\partial T}\right)_P \qquad (30)$$

The Anderson–Grüneisen parameter δ is distinguished from the Moelwyn-Hughes parameter C_1 by introducing a new parameter θ as

$$\theta = (C_1 - \delta) \qquad (31)$$

or

$$\theta = 2(\Gamma_{ith} - \Gamma_{iba}) + 1$$
$$\text{from eqs. (11) and (29)} \qquad (32)$$

Beyer's nonlinearity parameter (B/A),[36] which is a particular combination of the temperature and pressure derivatives of the sound speed, may be expressed as

$$\frac{B}{A} = (2\rho U^2)\left(\frac{\partial \ln U}{\partial P}\right)_T + \left(\frac{2U^2\alpha T}{C_P}\right)\left(\frac{\partial \ln U}{\partial T}\right)_P$$
$$= (B/A)' + (B/A)'' \qquad (33)$$

The first term $(B/A)'$ in eq. 33 represents the relative increase in phase velocity due to pressure, whereas the second term $(B/A)''$ is the increase due to temperature.

Using eqs. (20) and (28), expression (33) for (B/A) becomes

$$(B/A) = 2K_{ith} - 2K_{iba}\bar{\Gamma}\alpha T$$
$$= 2K_{ith} - 2K_{iba}(\gamma - 1) \qquad (34)$$

in which the average thermodynamic Grüneisen parameter $\bar{\Gamma}$ involving sums over all normal modes is given by eq. (2).

In the case of polymers, the values of $\bar{\Gamma}$ and α are very small[2,4,37] and γ is very near to unity[37,38]; hence, the second term in eq. (34) may be neglected in comparison with the first term without introducing an appreciable error. Thus, eq. (34) gives

$$\left(\frac{B}{A}\right) \approx 2K_{ith} \qquad (35)$$

Sharma[39] derived an expression for K_{ith} in terms of Mie potential exponents (m, n) as

$$K_{ith} = -\left(\frac{\partial \ln U}{\partial \ln V_0}\right)$$
$$= (m + n + 3)/6 \ (\text{at } V = V_0) \qquad (36)$$

From eqs. (35) and (36), it follows that

$$\left(\frac{B}{A}\right)_0 = (m + n + 3)/3 = 2K_{ith} \qquad (37)$$

where $(B/A)_0$ is the value of (B/A) corresponding to volume V_0.

Sharma[39] obtained the pressure coefficient of the bulk modulus from the volume derivative of the relation[40] between the adiabatic bulk modulus and molar volume V:

$$C_1 = -\left(\frac{\partial \ln B_s}{\partial \ln V}\right)_T$$
$$= (m + n + 6)/3 \ (\text{at } V = V_0) \qquad (38)$$

Comparison of eqs. (35) and (38) yields a relation between the nonlinearity parameter $(B/A)_0$ and the Moelwyn-Hughes parameter C_1:

$$C_1 = \left(\frac{B}{A}\right)_0 + 1 = 2\Gamma_{ith} \qquad (39)$$

Equations (35) and (39) show that the Beyer parameter of nonlinearity, the Moelwyn-Hughes parameter, the Carnavale and Litovitz acoustical parameter, and the isothermal Grüneisen parameter for a polymer are not independent but all express the same physical quantity. Usually, the exponent m has the value of 6 and $n > m$ as cited by various workers.[3,40,41]

For $m = 6$, eq. (38) gives

$$n = 3C_1 - 12 = 3\left(\frac{B}{A}\right)_0 - 9 \qquad (40)$$

Using the expression[41] for the pressure coefficient of the velocity of propagation of the ultrasonic waves in a polymer, the isothermal acoustical parameter K_{ith} and fractional (available) volume is related as[13]

$$\left(\frac{V_a}{V}\right) = (K_{ith} + 1)^{-1} \qquad (41)$$

where $V_a = V - V_0$ is the expansion volume or free (available) volume of the molecules; V, the total volume; and V_0, the volume of closest molecular packing.[41]

Using eqs. (11) and (41), the fractional free (available) volume can be expressed in terms of C_1 as

$$\frac{V_a}{V} = \left[\frac{C_1 + 1}{2}\right]^{-1} \qquad (42)$$

The isochoric temperature derivative Δ of the sound speed or the internal pressure is a very important factor with significant influence on various thermoacoustic properties. Sharma[11] determined and discussed the significance of the internal pressure–temperature behavior in establishing correlations between the internal pressure P_i and the cohesive energy density ε. The molecular constant r as a measure of the isochoric acoustical parameter Δ is given by[11]

$$r = \frac{P_i}{\varepsilon} = (1 - \Delta)^{-1} \qquad (43)$$

in which

$$\Delta = -\left(\frac{AT}{2}\right) \qquad (44)$$

where

$$A = \left(\frac{\partial \ln P_i}{\partial T}\right)_V$$

Equations (43) and (44) may be rewritten as

$$A = -\left(\frac{2}{T}\right)\left(\frac{r-1}{r}\right). \qquad (45)$$

Haward and Parker[42] obtained an expression relating the isochoric temperature coefficient of volume expansivity α and internal pressure P_i (in the zero pressure limit) as

$$A = \left(\frac{\partial \ln P_i}{\partial T}\right) = 2\tilde{B}\left(\frac{\partial \ln \alpha}{\partial T}\right)_V \qquad (46)$$

From thermodynamic considerations, the temperature derivative of α at constant volume can be obtained as[9]

$$\left(\frac{\partial \ln \alpha}{\partial T}\right)_V = \left[\left(\frac{\partial \ln \alpha}{\partial T}\right)_P + \alpha B\left(\frac{\partial \ln \alpha}{\partial P}\right)_T\right]$$
$$= -\alpha[2 + (\alpha T)^{-1}] \qquad (47)$$

Equations (45)–(47) give the temperature coefficient of P_i at constant volume as

$$A = [2 + (\alpha T)^{-1}]D\tilde{B} \qquad (48)$$

where D denotes the quantity $[(\partial \ln P_i)/(\partial T)]_P = -2\alpha$ obtained earlier by Sharma.[18]

Equations (44), (48), and (12) yield a relation for Δ as

$$\Delta = \frac{-[2 + (\alpha T)^{-1}][(-2\alpha)(\tilde{V}^{C_1})^{-1}]_T}{2} \qquad (49)$$

Sharma[10,43,44] introduced a dimensional parameter S_0 as

$$S_0 = -\left(\frac{A}{2}\right)(3 + 4\alpha T)$$
$$= -\left(\frac{1}{2}\right)\left(\frac{\partial \ln P_i}{\partial \ln T}\right)_V (3 + 4\alpha T)$$

Table I Thermoacoustical Properties of Polymers at Low Temperatures

Temp (K)	α ($\times10^{-5}$ K^{-1})	C_1	$(B/A)_0$	V_a/V	n	$\hat{V}$	$\tilde{B}$	Δ	Γ_{ith}	Γ_{ich}	Γ_{iba}	δ	θ	Y	S_0
Polyethylene															
20.0	8.9	566.13	565.13	0.0035	1686.4	1.0017	0.3658	0.3671	282.57	-205.24	487.81	975.62	-409.49	0.1110	1.1039
80.0	10.7	121.17	120.16	0.0163	351.5	1.0085	0.3581	0.3642	60.08	-41.55	101.63	203.27	-82.10	0.1105	1.1051
253.0	13.7	33.23	32.23	0.0584	87.69	1.0338	0.3305	0.3534	16.11	-9.19	25.31	50.62	-17.39	0.1090	1.1090
273.0	18.3	24.41	23.41	0.0786	61.25	1.0483	0.3158	0.3473	11.70	-5.95	17.66	35.32	-10.90	0.1082	1.1114
298.0	24.8	17.96	16.96	0.1054	41.89	1.0704	0.2945	0.2945	8.4814	-3.57	12.05	24.11	-6.15	0.1070	1.1143
Polyethylene (low density)															
4.0	7.1	3525.46	3524.46	5.67×10^{-4}	10564.38	1.0002	0.3675	0.3677	1762.23	-1293.92	3056.15	6112.30	-2586.84	0.1110	1.1036
80.0	13.4	97.63	96.63	0.0202	280.89	1.0106	0.3556	0.3633	48.31	-32.89	81.20	162.41	-64.78	0.1104	1.1055
Polytetraflouroethylene															
4.0	6.8	3680.80	3679.80	5.43×10^{-4}	11030.41	1.0002	0.3675	0.3677	1839.90	-1351.06	3190.97	6381.94	-2701.13	0.1110	1.1036
20.0	7.7	69.28	68.28	0.0284	195.86	1.0152	0.3505	0.3613	34.144	-22.46	56.609	113.21	-43.92	0.1101	1.1063
260.0	19.5	24.12	23.12	0.0796	60.37	1.049	0.3151	0.3470	11.56	-5.84	17.407	34.81	-10.69	0.1082	1.1115
Polypropylene															
80.0	5.3	240.18	239.18	0.0082	708.56	1.0040	0.3629	0.3660	119.59	-85.33	204.93	409.86	-169.67	0.1108	1.1044
280.0	19.5	22.72	21.72	0.0843	56.163	1.0526	0.3115	0.3455	10.86	-5.328	16.188	32.38	-9.656	0.1080	1.1120
Polytrifluorochloroethylene															
20.0	4.1	1223.84	1222.84	0.0016	3659.53	1.0008	0.3669	0.3675	611.42	-447.20	1058.62	2117.25	-893.40	0.1110	1.1037
80.0	4.5	282.11	281.11	0.0070	834.34	1.0035	0.3637	0.3663	140.55	-100.76	241.31	482.63	-200.52	0.1109	1.1042
280.0	6.9	56.11	55.11	0.0350	156.35	1.0190	0.3463	0.3597	27.55	-17.62	45.18	90.36	-34.23	0.1099	1.1069
Polystyrene															
4.2	5.0	4766.23	4765.23	4.19×10^{-4}	14286.71	1.0002	0.3676	0.3677	2382.62	-1750.37	4132.99	8265.99	-3499.95	0.1110	1.1036
20.0	5.6	897.19	896.19	0.0022	2679.57	1.0011	0.3665	0.3673	448.09	-327.03	775.13	1550.26	-653.07	0.1110	1.1038
240.0	6.1	72.65	71.65	0.0271	205.97	1.0144	0.3518	0.3616	35.83	-23.70	59.53	119.06	-46.41	0.1102	1.1062
Poly(methyl methacrylate)															
4.2	4.2	5673.26	5672.26	3.52×10^{-4}	17007.80	1.0001	0.3676	0.3678	2836.13	-2084.05	4920.18	9840.37	-4167.11	0.1111	1.1036
77.0	4.3	306.36	305.36	0.0065	907.08	1.0033	0.3640	0.3664	152.68	-109.68	262.36	524.72	-218.36	0.1109	1.1042
240.0	4.6	94.92	93.92	0.0208	272.78	1.0169	0.3553	0.3631	46.96	-31.89	78.86	157.72	-62.79	0.1104	1.1055
Nylon-6															
4.2	4.3	5541.43	5540.43	3.60×10^{-4}	16612.29	1.0001	0.3676	0.3678	2770.21	-2035.55	4805.7	9611.54	-4070.11	0.1110	1.1036
77.0	4.4	299.49	298.49	0.0066	886.49	1.0033	0.3639	0.3664	149.24	-107.15	256.40	512.80	-213.31	0.1109	1.1042
240.0	5.9	74.97	73.97	0.0263	212.92	1.0140	0.3519	0.3698	36.98	-24.55	61.54	123.08	-48.11	0.1102	1.1061

Table I *(Continued)*

Temp (K)	α ($\times 10^{-5}$ K^{-1})	C_1	$(B/A)_0$	V_a/V	n	$\tilde{V}$	$\tilde{B}$	Δ	Γ_{ith}	Γ_{ich}	Γ_{iba}	δ	θ	Y	S_0
Nylon-6,6															
20.0	5.1	984.72	983.72	0.0020	2942.18	1.0010	0.3666	0.3674	491.84	-359.23	851.10	1702.20	-717.47	0.1110	1.1038
80.0	5.9	216.20	215.20	0.0092	636.61	1.0047	0.3624	0.3658	107.60	-76.51	184.11	368.23	-152.62	0.1108	1.1044
280.0	8.2	47.91	46.91	0.0408	131.75	1.0226	0.3424	0.3582	23.45	-14.60	38.06	76.12	-28.20	0.1097	1.1075
Nylon-7															
4.2	4.2	5673.27	5672.27	3.52×10^{-4}	17007.80	1.0002	0.3677	0.3678	2836.13	-2084.06	4920.19	9840.38	-4167.11	0.1111	1.1037
77.0	4.3	306.36	305.36	0.0065	907.08	1.0033	0.3641	0.3665	152.68	-109.68	262.36	524.72	-218.36	0.1109	1.1042
240.0	5.5	80.11	79.11	0.0247	228.33	1.0131	0.3530	0.3623	39.55	-26.45	66.00	132.00	-51.89	0.1103	1.1060
Nylon-6,10															
4.2	4.1	5811.53	5810.53	3.44×10^{-4}	17422.60	1.0062	0.3677	0.3678	2905.27	-2134.92	5040.19	10080.38	-4268.84	0.1111	1.1037
77.00	4.1	321.09	320.09	0.0062	951.28	1.0032	0.3642	0.3665	160.05	-115.10	275.15	550.29	-229.20	0.1109	1.1042
240.0	4.8	91.15	90.15	0.0217	261.46	1.0114	0.3548	0.3630	45.08	-30.51	75.59	151.17	-60.02	0.1104	1.1057
Nylon-11															
4.2	4.5	5295.34	5294.34	3.77×10^{-4}	15874.02	1.0002	0.3677	0.3678	2647.17	-1945.02	4592.19	9184.39	-3889.05	0.1111	1.1037
77.0	4.6	286.66	285.66	0.0070	847.99	1.0035	0.3638	0.3664	142.83	-102.43	245.27	490.53	-203.87	0.1109	1.1043
240.0	4.6	94.93	93.93	0.0285	272.78	1.0110	0.3553	0.3632	46.96	-31.90	78.86	157.72	-62.79	0.1104	1.1056
Nylon-12															
4.2	4.5	5295.34	5294.34	3.77×10^{-4}	15874.02	1.0002	0.3677	0.3678	2647.17	-1945.02	4592.19	9184.39	-3889.05	0.1101	1.1037
77.0	4.6	286.66	285.66	0.0069	847.99	1.0035	0.3638	0.3664	142.83	-102.43	245.27	490.53	-203.87	0.1109	1.1043
240.0	6.6	67.49	66.49	0.0292	190.46	1.0157	0.3501	0.3612	33.24	-21.80	55.04	110.09	-42.60	0.1102	1.1064
Poly(vinyl fluoride)															
4.2	4.6	5180.32	5179.32	3.86×10^{-4}	15528.95	1.0002	0.3677	0.3678	2589.66	-1902.71	4492.34	8984.73	-3804.42	0.1111	1.1037
77.0	4.7	280.66	279.66	0.0071	829.97	1.0036	0.3637	0.3663	139.83	-100.22	240.05	480.11	-199.45	0.1109	1.1043
240.0	5.2	84.48	83.48	0.0234	241.43	1.0124	0.3538	0.3626	41.74	-28.05	69.79	139.58	-55.11	0.1104	1.1058
Poly(vinyl fluoride)															
4.2	4.4	5415.59	5414.59	3.69×10^{-4}	16234.17	1.0002	0.3677	0.3678	2707.29	-1989.26	4696.56	9398.11	-3977.52	0.1101	1.1037
77.0	4.5	292.94	291.94	0.0068	866.81	1.0035	0.3639	0.3664	145.97	-104.74	250.71	501.42	-208.48	0.1109	1.1043
240.0	4.9	89.38	88.38	0.0221	256.15	1.0117	0.3545	0.3629	44.19	-29.86	74.05	148.10	-58.72	0.1104	1.1057
Poly-4-methylpentene-1															
4.2	6.7	3557.99	3556.99	5.62×10^{-4}	10661.98	1.0003	0.3676	0.3678	1778.50	-1305.89	3084.39	6168.77	-2610.78	0.1111	1.1037
77.0	7.0	189.87	188.87	0.0105	557.61	1.0054	0.3617	0.3656	94.43	-66.83	161.26	322.52	-132.65	0.1108	1.1046
240.0	8.2	55.17	54.17	0.0356	153.52	1.0194	0.3460	0.3596	27.09	-17.27	44.36	88.72	-33.54	0.1099	1.1070

$$= \Delta(3 + 4\alpha T)$$
$$= 3\Delta S^* \tag{50}$$

where

$$S^* = 1 + \tfrac{4}{3}(\alpha T) \tag{51}$$

Here Δ is given by eq. (49).

RESULTS AND DISCUSSION

The calculated values of C_1, $(B/A)_0$, V_a/V, n, $\tilde{V}$, $\tilde{B}$, Δ, Γ_{ith}, Γ_{iba}, Γ_{ich}, δ, θ, Y, and S_0 using eqs. (7)–(51) are presented in Table I for 16 polymers at different low temperatures. The necessary reliable input data on volume expansivity (α) at low temperatures are taken from the literature.[45] It may be observed from Table I that the Moelwyn-Hughes parameter C_1, the Beyer nonlinearity parameter $(B/A)_0$, the repulsive exponent n, the isothermal Γ_{ith} and isobaric Grüneisen parameter Γ_{iba}, the isothermal Anderson–Grüneisen parameter δ, and the Y parameter are found to decrease with increasing temperature. However, the other parameters, viz., the fractional free (available) volume V_a/V and the reduced isothermal bulk modulus $\tilde{B}$, are found to increase with increasing temperature. The value of C_1 is found to decrease with increasing temperature. It signifies the nonlinear variation of α with temperature. The values of the parameters C_1 and $(B/A)_0$ are quite close and their ratio is very close to unity.

The decreasing values of n with increasing temperature indicate the increase in the interatomic equilibrium distance, which is also reflected in other physical properties such as density, volume, and expansion coefficient. Higher values of n for polymers as compared to liquids are expected since the polymers are strongly anisotropic, and the anisotropy is exhibited by interchain vibrations.[4,40] Thus, the intermolecular forces through the repulsive exponent n seem to play a vital role in establishing a close correlation between the anharmonic and nonlinear properties in polymers.

The polymers that have strong forces along the chains and weak forces between the chains tend to be anharmonic with high values of the lattice Grüneisen parameter Γ_{ith}. Hartmann[3] and Curro[46] suggested earlier that the anharmonicity of energy or potential that gives rise to a pressure or volume de-

pendence of the normal mode frequency of molecular vibrations is also governed by thermal expansion and the number of internal degrees of freedom of the polymer. During volume expansion of the polymer with increasing temperature, more and more additional disorder is introduced, which resulted in the relative changes in molecular vibration frequency and molecular order and structure, making the polymer less anharmonic at high temperature than at lower temperature. The decrease in Γ_{ith} with temperature, arising due to large number of internal degrees of freedom and the nature of anharmonic interactions in a polymer, may be indicative of some kind of molecular ordering effect.

The concept of available (free) volume (V_a) is very important in introducing additional disorder and obtaining quantitative information about the liquid–glass transition in a polymer system.[47–49] It can be observed from Table I that the fractional free volume (V_a/V) for the polymers under investigation has a value of about 3.5×10^{-4}, on average, at temperature 4.2 K, and its value increases to ≈ 0.02 as the temperature is increased to 240 K or more. This suggests that the fractional free volume in polymers is less than that observed for hydrocarbon liquids[41] because of larger size of micromolecules as compared to hydrocarbon molecules.

The decreasing value of the Beyer nonlinearity parameter is attributed to the decrease in ultrasonic velocity with temperature. The isobaric Grüneisen parameter Γ_{iba} is found to be greater than the isothermal Grüneisen parameter Γ_{ith}.

The isothermal Anderson–Grüneisen parameter[31] (δ), which is an important parameter in the theory of temperature dependence of the bulk modulus of solids,[34] decreases with increase of temperature. The calculated values of the parameter θ, defined as the difference between C_1 and δ, are found to be negative. The magnitude of the negative value, however, decreases with increase of temperature, indicating that the Moelwyn-Hughes parameter C_1 is less than the Anderson–Grüneisen parameter δ at all temperatures. The isochoric Grüneisen parameter is also found to be negative for all the polymers under study.

It may be interesting to note that at the very low temperature region the reduced bulk modulus is approximately equal to the isochoric thermoacoustic parameter, i.e., $\tilde{B} \approx \Delta \approx 0.36$. However, it may be seen that the two parameters show a slight decrease in their values as the temperature is increased.

Equation (50) shows that the Sharma parameter S_0 is proportional to the product of A and $(3 + 4T)$. It is interesting to note that a large α corresponds

to a small absolute value of A for a polymer. However, the value of the term $(3 + 4\alpha T)$ increases with rise of temperature in such a way that S_0 tends to be independent of the value of α for the polymer. So, it has been observed that even though α is different for different polymers the Sharma parameter S_0 defined by eq. (50) exhibits, on average, a constant value of 1.10 ± 0.01 for the polymers examined presently, similar to molten alkali halides,[10] polymers,[15,50] liquid alkali metals, ionic crystals, liquids,[14] semiconductors,[56] liquid crystals,[52] fluid hydrogen isotopes,[53] etc. This confirms the earlier conclusion about the possibility of using eq. (50) to establish the universal constancy of S_0, which turns out to be remarkably constant for any system existing either in a liquid or in a solid state and is found to be independent of temperature variation and of the nature and state of the substance in the condensed phase. This suggests that the Sharma constant S_0 may be regarded as a molecular constant for the condensed phase. The constant S_0 seems to be analogous to the molecular constant as a measure of the ratio of the internal pressure and cohesive pressure, which has the average value of 1.11 ± 0.1 for simple nonpolar substances[54] in the condensed phase.

The present treatment offers a convenient means for establishing simple relations between various parameters describing the thermoacoustic, anharmonic, and nonlinear properties of polymers through the Moelwyn-Hughes parameter. The treatment has the distinct advantage of calculating various thermoacoustic parameters at low temperatures employing only the experimental volume expansivity data. This allows further understanding of the significance of fractional free volume, the repulsive ex-

List of Symbols

Parameter	Symbol and Defining Equation
α	Thermal expansion coefficient $\left[= \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_P\right]$
B/A	Beyer's nonlinearity parameter [eq. (33)]
U	Sound speed
B_s	Adiabatic bulk modulus $[= V(\partial P/\partial V)_s]$
B	Isothermal bulk modulus $[= V(\partial P/\partial V)_T]$
β_s	Adiabatic compressibility $[= (1/V)(\partial V/\partial P)_s]$
β	Isothermal compressibility $[= (1/V)(\partial V/\partial P)_T]$
V_a	Available volume
V_a/V	Fractional free volume
P, V	Pressure, volume
T	Absolute temperature
ρ	Density
$K(K_{iba})$	Rao exponent $[= (\partial \ln U/\partial \ln V)_P]$ [eq. (19)]
K_{ith}	Carnevale and Litovitz exponent [eq. (20)]
K_{ich}	Isochoric acoustical parameter $[= (K_{ith} - K_{iba})]$ [eq. (18)]
C_P, C_V	Isobaric and isochoric heat capacity
γ	Heat capacity ratio $(= C_P/C_V = B_s/B)$
$\bar{\Gamma}$	Thermodynamic Grüneisen parameter [eq. (2)]
Γ	Microscopic lattice Grüneisen parameter [eq. (1)]
$\Delta\nu$	Change in normal mode frequency [eq. (21)]
$C_{P,i}, C_{V,i}, \gamma_i, B_{s,i}$	Fraction of C_P, C_V, γ, and B_s that interacts with volume
C_1	Moelwyn-Hughes parameter, $[= (\partial B/\partial P)_T]$ [eq. (9)]
$\tilde{V}$	Reduced molar volume $(= V/V^*)$
$\tilde{B}$	Reduced isothermal bulk modulus $(= B/B^*)$ [eq. (12)]
B^*, V^*	Characteristic isothermal bulk modulus, volume
$\Gamma_{iba}, \Gamma_{ith}, \Gamma_{ich}$	Isobaric, isothermal, and isochroic acoustical parameters [eqs. (23)–(25)]
m, n	Mie potential exponents [eq. (36)]
P_i	Internal pressure $(= \alpha TB)$
r	Molecular constant
ε	Cohesive pressure $(= P_i/r)$

List of Symbols

Parameter	Symbol and Defining Equation
X	Parameter $(= \bar{\Gamma}/\Gamma)$ [eq. (5)]
Y	Parameter $[= (B_{s,i}/B) = (\gamma_i/\gamma)]$ [eq. (6)]
Z	Parameter $[= (C_{P,i}/C_P) = (C_{V,i}/C_V)(\gamma_i/\gamma)]$ [eq. (4)]
δ	Isothermal Anderson–Grüneisen parameter $[= (1/\alpha)(\partial \ln B/\partial T)_P]$ [eq. (30)]
E	Parameter $[= \{2 + (\alpha T)^{-1}(-2\alpha)\tilde{V}^{C_1}\}^{-1}$ [eq. (26)]
F	Parameter $= (2\alpha)$, [eq. (26)]
A	Isochoric temperature coefficient of internal pressure $[= (\partial \ln P_i/\partial T)_V]$ [eq. (44)]
Δ	Isochoric acoustical parameter [eq. (49)]
S_0	Sharma constant [eq. (50)]
S^*	Parameter $[= (1 + [(4\alpha T)/3])]$ [eq. (51)]

ponent of the intermolecular potential, and the S_0 parameter (its universal constancy and temperature invariance) in describing the anharmonic and nonlinear properties with regard to molecular structure, order, and interactions in polymers at low temperatures.

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