The relationship between the Grüneisen and other thermodynamic parameters and intermolecular forces in polymers

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A simple relationship between the Grüneisen parameter and Beyer's non-linearity parameter in the case of polymers has been obtained in terms of Mie potential parameters from the pressure dependence of bulk modulus. Using this simple model, it is shown that Beyer's parameter of non-linearity, Carnevale and Litovitz's acoustical parameter, Moelwyn–Hughes parameter and the Grüneisen parameter are all related to each other and express the same physical quantity for polymers. The contribution of interchain vibrations to the total specific heat and the specific heat ratio has been found from the Grüneisen parameter in case of twelve polymers. It is proposed that the dependence of the isobaric specific heat of polymeric materials on the interchain forces is stronger than of the isochoric specific heat.

Keywords Grüneisen parameter; Beyer's non-linearity parameter; Moelwyn–Hughes parameter; interchain specific heat; bulk modulus; polymer

INTRODUCTION

New interest has been revived in the study of the Grüneisen parameter, first introduced by Grüneisen[1] to describe the equation of state and the molecular motions in solids, since the work of Anderson[2] who demonstrated the importance of the parameter in the theory of temperature dependence of the bulk modulus[3]. However, the Grüneisen parameter can be determined either from the temperature or pressure dependence of bulk modulus[3–9] and also from the internal pressure–temperature behaviour[10–11] in describing thermo-acoustic properties of polymers. It has been found to be a useful tool in describing interchain interactions, molecular structure and other thermo-acoustic properties[6,8,12–15] and 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[6].

Warfield[8] has pointed out that in polymers there are two distinct modes of lattice vibrations, viz. the interchain (low frequency and anharmonic) vibrations involving van der Waals bonds, and the intrachain (high frequency and harmonic) vibrations involving 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[12,14]. Hence. calculated values governed by these interchain vibrations determine the microscopic or lattice Grüneisen parameter while calculations dependent on all modes, both interchain and intrachain, on average give the thermodynamic Grüneisen parameter. Much confusion has existed in the literature by the failure to recognize the difference between the two types of Grüneisen parameter. However, in recent years, these have been related to the ratio of interchain-to-intrachain mode vibrations in case of polymers[6–8,10,12] and some work has been done in relating them to polymer structure[15]. In the study of ultrasonic properties of liquids, Rao's acoustical parameter[17] and Beyer's non-linearity parameter[18] are very important parameters for investigating the physico-chemical behaviour with regard to the association and non-linear effects[18–20] in liquids which occur due to the passage of high amplitude sound waves through liquids. The constancy of the Rao's acoustical parameter and that of Carnevale and Litovitz[21] has taken as a criterion for organic liquids being unassociated[17,19,22] but fails in the case of compressed liquefied gases[9,19,23–27] and liquid metals[28]. However, the non-linearity parameter of liquids provides some important information about the physical attributes of the liquid such as internal pressure, intermolecular spacing and acoustic scattering[22].

Yamamoto and Wada[29] extended the study of Rao's acoustical parameter to polymers. Approaching polymers from the point of view of simple solids and also from the results for liquids, Warfield and Hartmann[4] have shown that the two disparate approaches are equivalent and that the Grüneisen parameter, Rao's acoustical parameter and Anderson–Grüneisen parameter are all related to each other. Similar results have been obtained by Sharma[10] based on the assumption that the temperature and pressure derivatives of the compressibility (reciprocal of bulk modulus) are not independent but are related through their effect on the volume. Recently, Hartmann[30] has attempted to show theoretically, on the basis of intermolecular potential energy considerations, and the assumption that the temperature and pressure derivatives of the sound speed are identical, that Beyer's non-linearity parameter, Rao's acoustical parameter and the Grüneisen parameter of liquids are all simply related to each other. Another quantity of current interest is the Moelwyh–Hughes parameter[31] expressing the pressure coefficient of bulk modulus and serving as a test of the equation of state

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of liquids, which is an important parameter as it is related to molecular force constants governing the potential energy and other thermodynamic properties of liquids[9,26,27,32,33], but has recently been shown to be useful in studying polymers[10]. In view of these observations it is of interest to analyse possible theoretical foundations of these inter-relationships by extending the study in case of polymers by correlating the Grüneisen parameter to the Beyer's non-linearity parameter, Anderson–Grüneisen parameter, Moelwyn-Hughes parameter through the acoustical parameters by Rao and Carnevale and Litovitz. The properties of interest are the bulk modulus and the sound speed whose temperature and pressure dependence may be conveniently utilized to obtain such relationships.

THERMO-ACOUSTICAL PARAMETERS

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

$$\Delta C=\left(\frac{\partial C}{\partial T}\right)\Delta T+\left(\frac{\partial C}{\partial V}\right)_T\Delta V \tag{1}$$

where C is the bulk ultrasonic velocity, V is the molar volume at absolute temperature T.

Using the thermodynamic relationship[34]

$$\alpha B_s\left(\frac{\partial \ln C}{\partial p}\right)_T=\left[\left(\frac{\partial \ln C}{\partial T}\right)_V-\left(\frac{\partial \ln C}{\partial T}\right)_p\right] \tag{2}$$

it follows that

$$K=K'+K'' \tag{3}$$

in which the isobaric, isothermal and isochoric acoustical parameters are defined as

$$K=-\left(\frac{\partial \ln C}{\partial \ln V}\right)_p=-\left(\frac{1}{\alpha}\right)\left(\frac{\partial \ln C}{\partial T}\right)_p \tag{4}$$

$$K'=-\left(\frac{\partial \ln C}{\partial \ln V}\right)_T=B_s\left(\frac{\partial \ln C}{\partial p}\right)_T \tag{5}$$

$$K''=-\left(\frac{1}{\alpha}\right)\left(\frac{\partial \ln C}{\partial T}\right)_V=-B_s\left(\frac{\partial \ln C}{\partial p}\right)_V \tag{6}$$

where α and B_s are respectively the volume expansivity and the adiabatic bulk modulus and p is the pressure. Equations (4) and (5) are normally used to represent the acoustical parameters of Rao[17], and Carenevale and Litovitz[21], respectively.

Assuming that the bulk modulus of a polymer depends only on volume[6,35], the isobaric and isothermal Grüneisen parameters can be determined either by using temperature measurements or pressure measurements with the relations[6-8,35]

$$\Gamma=-\left(\frac{1}{2\alpha}\right)\left(\frac{\partial \ln B_s}{\partial T}\right)_p \tag{7}$$

$$\Gamma'=\left(\frac{1}{2}\right)\left(\frac{\partial B_s}{\partial p}\right)_T \tag{8}$$

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

$$C=(B_s/\rho)^{\frac{1}{2}}. \tag{9}$$

where ρ is the density.

Using equation (9) in equations (4) and (7), we obtain

$$\delta=2K+1=2\Gamma \tag{10}$$

where δ is the Anderson–Grüneisen parameter given by[3,4]

$$\delta=-\left(\frac{1}{\alpha}\right)\left(\frac{\partial \ln B_s}{\partial T}\right)_p \tag{11}$$

Wada[36] and Moelwyn-Hughes[32] defined a parameter for liquids as

$$C_1=\left(\frac{\partial B_s}{\partial p}\right)_T=-\left(\frac{\partial \ln B_s}{\partial \ln V}\right)_T=B_s\left(\frac{\partial \ln B_s}{\partial p}\right)_T \tag{12}$$

Using equations (5), (8) and (9) it is easy to show

$$C_1=2K'+1=2\Gamma' \tag{13}$$

Equation (10) resembles relations obtained by Warfield and Hartmann[4], and Sharma[10] for polymers. In this order of approximation, Warfield and Hartmann[4] have neglected the $\frac{1}{2}$ factor and have expressed the results of equation (10) in the form

$$\Gamma\approx(\tfrac{1}{2})\delta\approx K \tag{14}$$

Equation (10) supports the empirical findings of Rao[17] and equation (13) explains those of Carnevale and Litovitz[21] as confirmed by other workers[4,10,28,33]. This shows that the isobaric Grüneisen parameter is essentially the same as Rao's acoustical parameter and the isothermal Grüneisen parameter corresponds to the Carnevale and Litovitz's parameter.

POTENTIAL FUNCTION: SPECIFIC RESULTS

It might also be interesting to obtain expressions for these thermo-acoustical parameters in terms of Beyer's non-linearity parameter[18] and Mie potential parameters.

The Mie potential is usually represented by the bi-reciprocal function given by[16,30,32]

$$U=aV^{-n/3}-bV^{-m/3}, n>m. \tag{15}$$

where U is the intermolecular potential for a system of molar volume V,m,n are Mie potential exponents and a,b are Mie potential parameters.

Using equation (15), the bulk sound speed (squared) becomes[30,32]

$$\frac{C^2}{U_0}=\frac{mn}{g(n-m)}\left[(n+3)\left(\frac{V}{V_0}\right)^{-n/3}-(m+3)\left(\frac{V}{V_0}\right)^{-m/3}\right. \tag{16}$$

where U_0 and V_0 represent the values of U and V

respectively at zero temperature and pressure.

The pressure dependence of the sound speed follows from the volume derivative of equation (16) at constant temperature as

$$-\left(\frac{\partial \ln C}{\partial \ln V}\right)=\frac{\left(\frac{1}{6}\right)\left[m(m+3)-n(n+3)\left(\frac{V}{V_0}\right)^{-(n-m)/3}\right]}{\left[(m+3)-(n+3)\left(\frac{V}{V_0}\right)^{-(n-m)/3}\right]} \qquad (17)$$

At $V=V_0$, this derivative using equation (5) becomes

$$K'=-\left(\frac{\partial \ln C}{\partial \ln V_0}\right)=(m+n+3)/6 \qquad (18)$$

Equation (18) gives a result which is almost identical to the result found by Schuyer[37] and was essentially first derived by Moelwyn-Hughes[31]. However, equation (18) is exactly identical to the result found by Pastine[38] for the expression of the microscopic Grüneisen parameter proposed by Dugdale and MacDonald[39] by taking into account the variation of Poisson's ratio with volume.

Haward and MacCallum[16] give the following relation between the adiabatic bulk modulus and molar volume V as

$$B_s=\frac{B_0}{(n-m)}\left[(n+3)\left(\frac{V}{V_0}\right)^{-(n+3)/3}-(m+3)\left(\frac{V}{V_0}\right)^{-(m+3)/3}\right] \qquad (19)$$

where B_0 is the adiabatic bulk modulus corresponding to the volume V_0.

The pressure dependence of the bulk modulus follows from the volume derivative of equation (19) as

$$C_1=-\left(\frac{\partial \ln B_s}{\partial \ln V}\right)_T=$$

$$\frac{\left(\frac{1}{3}\right)\left[(n+3)^2\left(\frac{V}{V_0}\right)^{-(n+3)/3}-(m+3)^2\left(\frac{V}{V_0}\right)^{-(m+3)3}\right]}{\left[(n+3)\left(\frac{V}{V_0}\right)^{-(n+3)/3}-(m+3)\left(\frac{V}{V_0}\right)^{-(m+3)/3}\right]^{-1}} \qquad (20)$$

At $V=V_0$, this derivative, using equation (12) becomes:

$$C_1=(m+n+6)/3 \qquad (21)$$

Equation (21) gives the same result as obtained by Molewyn-Hughes[32]. Combining equations (18) and (21), it can be seen that equation (13) is obtained. This shows that equation (13) represents the correct relationship between the parameter C_1 and K'. In deriving all these expressions, the isothermal and adiabatic bulk modulus for a polymer have been assumed as being identical since their ratio, which is equal to the specific heat ratio γ, does not vary with volume and is very near to unity for a hard rigid and crosslinked polymer[40]. This assumption has been justified by other workers for solids[41-43] and polymers[4,8,9,35] at ordinary temperatures and pressures. However, to the first approximation[9,30,33,44], volume independence of γ for liquids has also been suggested.

Relationship between non-linearity parameter and thermo-acoustic parameters

Beyer's non-linearity parameter $\left(\frac{B}{A}\right)$, which is a particular combination of the temperature and pressure dependence of the sound speed is given by[18]

$$\left(\frac{B}{A}\right)=2\rho C\left(\frac{\partial C}{\partial p}\right)_T+\frac{2CT\alpha}{C_p}\left(\frac{\partial C}{\partial T}\right)_p. \qquad (22)$$

Using equations (5) and (9), expression (22) for $\left(\frac{B}{A}\right)$ becomes

$$\left(\frac{B}{A}\right)=2K'-2K\bar{\Gamma}\alpha T=2K'-2K(\gamma-1) \qquad (23)$$

in which the average thermodynamic Grüneisen parameter $\bar{\Gamma}$ involving sums over all normal modes is given by[5,45]

$$\bar{\Gamma}=\frac{\alpha C^2}{C_p}=\frac{(\gamma-1)}{\alpha T} \qquad (24)$$

where C_p is the specific heat at constant pressure.

In the case of polymers, the values of $\bar{\Gamma}$ and α are very small[6,8,46] and γ is very near to unity[40,46], hence the second term in equation (23) may be neglected in comparison with the first term without introducing any appreciable error. Thus equation (23) gives

$$\left(\frac{B}{A}\right)\approx 2K' \qquad (25)$$

Using equations (18) and (25) one obtains

$$\left(\frac{B}{A}\right)_0=(m+n+3)/3=2K' \qquad (26)$$

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

Comparison of equations (21) and (26) yields a relation between the non-linearity parameter $\left(\frac{\mathrm{B}}{\mathrm{A}}\right)_0$ and the Moelwyn-Hughes parameter C_1

$$C_1=\left(\frac{B}{A}\right)_0+1=2\Gamma' \qquad (27)$$

Equations (25) and (27) show that Beyer's parameter of non-linearity, Moelwyn-Hughes parameter, Carnevale and Litivitz's acoustical parameter and the isothermal Grüneisen parameter for a polymer are not independent but all express the same physical quantity.

Interchain specific heat

For metal and ionic crystals[5], liquid mercury and liquid metals[9,15,32] and liquified gases[24,27], the approximate relationship $\Gamma'\approx\bar{\Gamma}$ holds but this is not true for polymers[6,8,35,40,47] and complex liquids[28] comprising unsymmetrical molecules with strong polar interactions and hydrogen bonding effects.

Following the suggestion of Wada *et al.*[12] for establishing a corresponding relationship between Γ' and $\bar{\Gamma}$, Warfield[8] and Haward[47] have obtained a quantity given by

$$X=\left(\frac{\bar{\Gamma}}{\Gamma'}\right)=\left(\frac{C_{v,i}}{C_v}\right) \qquad (28)$$

As pointed out by Wada *et al.*[12], Warfield[8] and Haward[47], the quantity X is of some interest since it measures the ratio $C_{v,i}/C_v$ where $C_{v,i}$ is the interchain specific heat and is that part of the specific heat taken up by molecular vibrations which interact within a constant volume and C_v is the total (calorimetric) specific heat at constant volume.

In view of these observations and suggestions it would be interesting to calculate the interchain vibrations contribution $C_{p,i}$ to the total isobaric specific heat C_p from the relation

$$C_{p,i}/C_p=(\gamma_i/\gamma)(C_{v,i}/C_v) \qquad (29)$$

in which

$$\gamma_i=C_{p,i}/C_{v,i}$$

Comparing equations (28) and (29) it follows that

$$Y=(\gamma_i/\gamma)X \qquad (30)$$

in which

$$Y=C_{p,i}/C_p \qquad (31)$$

where γ_i using the relation (24) may be written as

$$\Gamma_i=\Gamma'=(\gamma_i-1)/\alpha T \qquad (32)$$

where the subscript i refers to interchain and $\Gamma_i=\Gamma'$.

Equation (30) may be rewritten as

$$Z=Y/X=(\gamma_i/\gamma) \qquad (33)$$

Equations (28) and (30) are more useful as a method of obtaining $C_{v,i}$ and $C_{p,i}$, than of calculating Γ_i since its values are not readily obtained. Equation (30) reduces to that obtained by Hartmann[35] for $\gamma_i=\gamma$ or $Z=1$. If it were true that $\gamma_i=\gamma$, then equations (24), (28) and (32) render $\bar{\Gamma}=\Gamma_i=\Gamma'$ which is not true in case of polymers[6,8,12,47]. Thus equation (30) gives a general, correct form of the relation between $C_{p,i}$ and the Grüneisen parameter for technical purposes. Since values of Γ' are several times more than those of $\bar{\Gamma}$ in polymers[6,8,12,40,47], it might be expected that $\gamma_i>\gamma$ for a polymer.

RESULTS AND DISCUSSION

Calculated values of the parameters K', C_1, $\left(\frac{B}{A}\right)_0$, γ, γ_i and the quantities X, Y and Z of several polymers, using equations (13), (24), (27), (28), (30), (32) and (33) from the data on $\bar{\Gamma}$ and Γ' using equations (8) and (24) as reported by Warfield[8], Wada *et al.*[12] and Hartmann[6,7,35] are presented in *Table 1*. Necessary additional experimental data on α for calculating γ and γ_i are taken from the values as cited by various workers[35,46,48–50]. The calculated values of Γ' range from ~3 to 9 while those of $\left(\frac{B}{A}\right)_0$ from ~6 to 17 in case of polymers presently under investigation. The quantity X representing a ratio of that portion of the isochoric specific heat due to interchain vibrations to the total isochroic specific heat has a maximum value of 0.29 in the case of poly(phenyl quinoxaline) and a minimum value of 0.05 for poly(tetrafluoroethylene). This value in the case of poly(phenyl quinoxaline) is at the high end of the range for polymers[6,8,35,47] presumably because the bulky side group in this polymer is capable of many different normal modes of vibrations. An inspection of *Table 1* reveals the importance of the factor Z representing the ratio of the interchain to the total specific heat ratio which has a significant contribution ranging from ~1.2 to 1.5 to the interchain isobaric specific heat in most of the polymers

Table 1 Calculated values of Grüneisen parameter, Beyer's non-linearity parameter and interchain specific heat of polymers

Polymer	T (K)	α (10^{-4} K^{-1})	$\bar{\Gamma}$	Γ'	K'	C_1	$\left(\frac{B}{A}\right)_0$	γ	γ_i	X	Y	Z
Phenolic polymer	303	3.1	1.3	6.3	5.8	12.6	11.6	1.12	1.59	0.21	0.29	1.42
Poly(phenyl quinoxaline)	303	2.6	1.0	3.5	3.0	7.0	6.0	1.08	1.28	0.29	0.34	1.18
Polystyrene	298	2.33	0.79	4.4	3.9	8.8	7.8	1.06	1.31	0.18	0.22	1.24
Poly(methyl methacrylate)	298	2.1	0.82	4.0	3.5	8.0	7.0	1.05	1.25	0.20	0.24	1.19
Polyethylene (high density)	298	5.0	0.52	4.1	3.6	8.2	7.2	1.08	1.49	0.13	0.19	1.49
Polypropylene (isotactic)	298	4.8	0.96	9.0	8.5	18.0	17.0	1.12	2.29	0.09	0.18	2.04
Polyoxymethylene	298	2.43	0.51	5.6	5.1	11.2	10.2	1.04	1.40	0.09	0.12	1.35
Poly(4-methyl pentene-1)	298	3.8	1.07	5.0	4.5	10.0	9.0	1.12	1.57	0.21	0.29	1.40
Poly(ethylene oxide)	298	3.3	1.02	5.0	4.5	10.0	9.0	1.10	1.49	0.20	0.27	1.36
Polybutene-1	298	4.5	0.66	4.6	4.1	9.2	8.2	1.09	1.62	0.14	0.21	1.49
Poly(chlorotrifluoroethylene)	298	8.1	0.36	6.1	5.6	12.2	11.2	1.09	2.47	0.06	0.14	2.27
Poly(tetrafluoroethylene)	298	1.35	0.40	8.0	7.5	16.0	15.0	1.02	1.32	0.05	0.06	1.29

being presently studied. The present results confirm the proposal of Haward and MacCallum[16] that the adiabatic bulk modulus of a polymeric glass is determined by interchain forces. A polymer glass well below the glass transition temperature T_g and at short times offers a particularly favourable case.

This shows that the interchain vibrations contributions to C_p are much higher than those in case of C_v. It is concluded that the molecular vibrations have a stronger effect on C_p than C_v of a polymer. Once the interchain specific heat has been separated out, it is convenient to describe the dependence of the thermal expansion[14,47,52], thermal conductivity[52], adiabatic bulk modulus[16,47] and ultrasonic absorption[6] of a non-conducting medium on the interchain forces and also employ the concept of interchain specific heat to test[8] the usefulness of various polymeric solid state theories.

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