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ON THE EVALUATION OF THERMO-ACOUSTIC AND NON-LINEAR PROPERTIES OF POLYMERS AND LIQUIDS

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Thermo-acoustic properties of polymers are calculated in terms of the temperature and pressure derivatives of the bulk modulus on the basis of an assumption that the isochoric temperature coefficient of the bulk modulus is an important factor. An attempt has made to obtain correlations between the thermoacoustic, anharmonic and nonlinear properties with the molecular force constants governing the intermolecular potential. These properties have been expressed in terms of the volume expansion which is found as the controlling factor for their dependence on temperature and volume for liquids.

1. Introduction

New interest has been revieved in the study of the GRÜNEISEN parameter Γ, the ANDERSON-GRÜNEISEN parameter δ and the MOELWYN-HUGHES parameter C_1 in the view of the temperature and pressure coefficient of the bulk modulus (the reciprocal of compressibility) as an extension to molten state, polymers and liquids [1–7]. The MOELWYN-HUGHES parameter C_1, expressed as the pressure coefficient of bulk modulus, serves as a severe test of the equation of state and is an important thermodynamic quantity in studying the molecular-thermodynamic, surface and thermo-acoustic properties [4–7]. The temperature dependence of the bulk modulus is usually described by the ANDERSON-GRÜNEISEN parameter δ which is found to be useful for describing the microscopic behaviour, internal structure and other related properties [2], [3], [6], [8]. The GRÜNEISEN parameter Γ, as a measure of anharmonicity of molecular vibrations, has also been related to the ratio of inter-chain to intra-chain normal mode vibrations, and it serves as an effective guide in determining the mechanism of ultrasonic absorption and in establishing a correlation with the results of phonom – phonom interaction absorption [7], [9]–[11]. The present paper deals with the correlations between these parameters with the molecular force constants governing the intermolecular potential, through the isobaric, isothermal and isochronic acoustical parameters by RAO [12], CARNEVALE and LITOVITZ [13] and SHARMA [14]. The properties of interest are the bulk modulus, volume expansion and the sound speed, whose temperature and pressure dependence may be conveniently utilized to obtain such relationships.

2. Relationship between the thermo-acoustical parameters and intermolecular potential functions

Assuming the sound speed as a function of both volume and temperature, the isobaric, isothermal and isochronic acoustical parameters are related as [11], [14]

$$K' = K + K'' \tag{1}$$

in which

$$K'' = (K' - K) = \left(\frac{1}{a}\right)\left(\frac{d\ln C}{dT}\right)_V, \tag{2}$$

$$K = -\left(\frac{1}{a}\right)\left(\frac{d\ln C}{dT}\right)_P, \tag{3}$$

$$K' = B\left(\frac{d\ln C}{dP}\right)_T, \tag{4}$$

$$C^2 = BV, \tag{5}$$

where K and K' respectively represent the isobaric and isothermal acoustical parameters due to RAO [12], and that of CARNEVALE and LITOVITZ [13] and K'' is the isochoric acoustical parameter due to SHARMA [14]. C is the bulk sound speed, B is the bulk modulus, a is the volume expansion and V is the specific volume at pressure p and absolute temperature T.

Following SCHUYER [15], the RAO's isobaric acoustical parameter may be expressed as

$$K = (m + n + 1)/6, \tag{6}$$

where m and n are respectively the attractive and repulsive exponents of the intermolecular potential.

The expression for the ANDERSON-GRÜNEISEN parameter δ as obtained by BARKER [16] may be expressed in terms of m and n as

$$\delta = -\left(\frac{1}{a}\right)\left(\frac{d\ln B}{dT}\right)_p = (m + n + 4)/3. \tag{7}$$

From equations (6) and (7) it follows that [4]

$$\delta = 2K + 1 = 2\Gamma \tag{8}$$

in which the GRÜNEISEN parameter Γ is given by the temperature dependence of the bulk modulus as [4], [17],

$$\Gamma = -\left(\frac{1}{2\alpha}\right)\left(\frac{d\ln B}{dT}\right)_p . \tag{9}$$

Equation (8) resembles the relation obtained by warfield and HARTMANN [1] and SHARMA [4, 5].

The expressions for parameters K' and C_1 may be expressed as [4]

$$K' = (m+n+3)/6, \tag{10}$$

$$C_1 = \left(\frac{dB}{dp}\right)_T = 2K' + 1 = \frac{m+n+6}{3} \tag{11}$$

BEYER'S parameter of nonlinearity (B/A) which is a particular combination of the temperature and pressure derivatives of the sound speed has been shown by SHARMA [4] to be related to K' at $V = Vo$ by the relation

$$(B/A)_0 = (C_1 - 1) = (m+n+3)/3 = 2K', \tag{12}$$

where $(B/A)_0$ is the value of (B/A) corresponding to the specific volume Vo which represents the value of V at zero temperature and pressure.

Usually the exponent m has the value of 6 and $n > m$ for substances [6], [19]. The value of n varies from about 13 to 19 for quasispherical, unassociated molecular liquids [6], [19].

For $m = 6$, equations (7) and (8) give

$$n = 3(\delta - 4) + 2 = 6K - 7 = 6\Gamma - 10. \tag{13}$$

Equations (7) and (12) lead to the relation between δ and $(B/A)_0$ as

$$\delta = \left(\frac{B}{A}\right)_0 + \frac{1}{3}. \tag{14}$$

Equations (13) and (14) establish the direct and close relationship between Γ, $(B/A)_0$ and n which can be expressed in terms of δ for a polymer. This suggests that the GRÜNEISEN parameter Γ as a measure of anharmonicity of molecular vibrations is related to the parameter $(B/A)_0$ describing the non-linearity effects in polymers. Thus intermolecular forces through the repulsive exponent n seem to play a vital role in establishing a close correlation between the anharmonic and nonlinear properties of the polymer.

Assuming the bulk modulus as a function of both volume and temperature, it can be shown from the thermodynamic considerations [11] that

$$\alpha B\left(\frac{d\ln B}{dp}\right)_T = \left[\left(\frac{d\ln B}{dT}\right)_v - \left(\frac{d\ln B}{dT}\right)_p\right]. \tag{15}$$

From equations (2), (5), (7) (11) and (15) it follows that

$$\left(\frac{d\ln B}{d\ln T}\right)_v = (C_1-\delta)\alpha T = 2K''\alpha T. \tag{16}$$

Since the values of δ are greater than C_1, hence the isochronic acoustical parameter K'' is a negative quantity for polymers [11], while it is a positive quantity for liquids [14]. It implies that the bulk modulus should decrease with the rise of temperature at a constant volume in a polymer.

This implies that volume changes caused by temperature have a greater effect on bulk modulus or sound speed than volume changes caused by pressure in the polymer.

The relation between the isothermal acoustical parameter K' and free volume [20] may be expressed in terms of n, using equations (10) and (11), as

$$Va/V = (K'+1)^{-1} = \frac{2}{(C_1+1)} = 6/(n+15), \tag{17}$$

where $Va = (V-Vo)$ is the free volume, V is the volume at absolute temperature T and V_0 is the volume of the polymer at 0 K.

Equations (7)–(9), (11), (13), (14), (16) and (17) allow direct evaluation of the parameters δ, C_1, Γ, K, K', K'', n, $(B/A)_0$, $(d\ln B/d\ln T)_v$ and Va/V from the available data for the thermo-acoustic parameters involved. Such calculations for eight polymers are presented in Table 1 using the calculated values of K, K' and K'' and the experimental data for volume expansion α from [11]. The calculated values of $(B/A)_0$ for most of the polymers are of the same order as those observed for fluorocarbon fluids [21]. However, the values of n vary from about 16 to 56 which is more than range of about 16 to 19 for quasi-spherical

Table 1. Calculated values of thermo-acoustic parameters of polymers

Polymer	T [K]	Γ	δ	C_1	$\left(\frac{B}{A}\right)_0$	$\left(\frac{d\ln B}{d\ln T}\right)_v$	n	Va/V
Phenolic polymer	303	7.6	15.2	12.6	14.9	−0.24	35.6	0.14
Polyphenyl quinoxaline	303	4.4	8.8	7.0	8.5	−0.14	16.4	0.25
Polymethyl methacrylate	298	4.8	9.8	8.0	9.3	−0.10	18.8	0.22
Polystyrene	298	4.4	8.8	8.8	8.5	−0.0	14.4	0.20
Polyethylene (high density)	298	5.1	10.2	8.2	9.9	−0.30	20.6	0.22
Polypropylene	298	11.0	22.0	18.0	21.7	−0.57	56.0	0.10
Polymethylene Oxide	298	6.3	12.6	11.2	12.3	−0.10	27.8	0.16
Poly(4-methyl pentene-1)	298	5.1	10.2	10.0	9.9	−0.02	20.6	0.18

molecular liquids [19]. Higher values of n for polymers as compared to liquids are expected since the polymers are strongly anisotropic and the anharmonicity is exhibited by interchain vibrations [9–11, 17]. The calculated values of (Va/V) for polymers under present investigation range from about 0.10 to 0.25 as compared to about 0.15 for fluorocarbon fluids [10] and 0.20 for saturated hydrocarbon fluids [19].

3. Computation of thermo-acoustical parameters of liquefied gases

Pastine [22] related the anharmonic parameter Γ in terms of the exponents m and n as

$$\Gamma = (m+n+3)/6. \tag{18}$$

Equation (18) for Γ resembles the equation (10) obtained for K' by Sharma [4].

Using equations (7), (8), (11), (14) and (18), the parameters $(B/A)_0$, K, δ and C_1 of a liquid may be expressed in terms of Γ as

$$\left(\frac{B}{A}\right)_0 = \delta - \left(\frac{1}{3}\right) = (C_1 - 1) = 2\Gamma = 2\left(K + \frac{1}{3}\right). \tag{19}$$

The parameter Γ can be estimated from the expression obtained for the Debye temperature for a liquid [23]. It has been shown [23] that the GRÜNEISEN parameter Γ can be expressed in terms of volume expansion of the liquid as

$$\Gamma = 1 + (2\alpha T)^{-1}. \tag{20}$$

Equations (19) and (20) lead to the expression for δ, K and $(B/A)_0$ in terms of α as

$$\delta = \frac{7}{3} + (\alpha T)^{-1}, \tag{21}$$

$$K = 2/3 + (2\alpha T)^{-1}, \tag{22}$$

$$\left(\frac{B}{A}\right)_0 = 2 + (\alpha T)^{-1}. \tag{23}$$

Equations (20)–(23) show that the volume expansion α is the controlling factor the dependence of the parameters Γ, δ and K of liquids on temperature and volume. For simple liquids these parameters are found to decrease with a rise in temperature [5], [24].

Equations (20) and (22) establish a direct relationship between Γ and K for liquids which can be expressed in terms of α only. This result agrees closely with the suggestion of HARTMANN [25] that the same anharmonicity of the intermolecular potential that gives rise to a volume or temperature dependence of normal mode frequency also produces thermal expansion, so it is not surprising that Γ and α are related.

The temperature dependence of the parameter δ of a liquid can be treated qualitatively by considering equation (21) which yields the temperature derivatives of δ as

$$\left(\frac{\partial \delta}{\alpha T}\right)_p = -\left(\frac{\delta}{T}\right)\left[1+\frac{4/\delta}{3\,\delta-7}\right], \tag{24}$$

where the isobaric temperature derivative of α is given by [11], [14]

$$\left(\frac{d\ln\alpha}{dT}\right)_p = \frac{\alpha}{3}\,(7+4\,\alpha T).$$

Equation (24) correctly predicts a negative coefficient $(\partial\delta/\alpha T)_p$ showing a decrease in δ with a rise of temperature. This consequence is in qualitative accordance with the similar behaviour of K, Γ and C_1 observed for simple liquids [5], [9], [24].

The calculated values of Γ, δ, K and $(B/A)_0$ using equations (20)–(23) for several liquefied gases are presented in Table 2. Experimental data on α needed for the calculations were taken from literature [2–29]. The values of parameters δ and $(B/A)_0$ vary from about 4 to 5.5 and those of K around 2 in the case of the liquefied gases under present investigation. A similar pattern has also been observed earlier for simple liquids [8], [23], [24].

Table 2. Calculated values of the parameters K and (B/A) of liquefied gases

Liquefied gas	T [K]	$\alpha\cdot10^3$ [K^{-1}]	Γ	δ	K	$(B/A)_0$
Argon	84	4.37	2.36	5.05	2.03	4.72
Nitrogen	70	5.16	2.39	5.11	2.06	4.78
Oxygen	85	4.33	2.36	5.05	2.03	4.72
Neon	27	14.6	2.27	4.88	1.94	4.54
Krypton	120	3.20	2.30	4.94	1.97	4.60
Xenon	165	2.26	2.34	5.02	2.01	4.68
Methane	112	3.34	2.34	5.02	2.01	4.68
Hydrogen	20	15.68	2.59	5.52	2.26	5.18
Parahydrogen	20	15.87	2.57	5.48	2.24	5.14
Butane	273	2.13	1.86	4.06	1.53	3.72
Ethane	184.5	2.40	2.13	4.57	1.80	4.26
Carbon monoxide	81.6	5.27	2.16	4.66	1.83	4.32
Sulphur dioxide	263	1.70	2.12	4.58	1.79	4.24
Carbon dioxide	289	13.75	2.26	4.86	1.93	4.52
Hydrogen chloride	188	2.40	2.11	4.56	1.78	4.22
Hydrogen iodide	238	1.44	2.46	5.26	2.13	4.92

4. Conclusions

From the considerations presented in this paper the following conclusions can be drawn:

1. The isobaric temperature and isothermal pressure derivatives of the bulk modulus or the sound speed are not independent but are related through their isochoric pressure or temperature derivatives.

2. The anharmonic and nonlinear properties of a polymer can be described in terms of temperature and pressure dependence of the bulk modulus.

3. The repulsive exponent of the intermolecular forces in a polymer seems to play a vital role in establishing a close correlation between the anharmonic and the nonlinear properties of the polymer.

4. Equation (17) makes possible the evaluation of (Va/V) of a polymer from the repulsive exponent calculated from the velocity and the pressure coefficient of the velocity of ultrasonic waves in the polymer.

5. Equations (20)–(23) make possible the evaluation of the anharmonic and the nonlinear properties of a liquid from the volume expansion alone showing a decrease with an increase in temperature.

6. The values of the parameters Γ and δ of a liquid are several times lower than that of a polymer, showing that polymers are strongly anisotropic and anharmonic as compared to liquids.

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