Isothermal volume derivative of thermodynamic Gruneisen parameter, nonlinearity parameter and intermolecular heat capacity of liquids

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Abstract: The isochoric temperature derivative of Sound Velocity, the isothermal volume derivative of thermodynamic Gruneisen parameter, fractional free (available) volume and the repulsive exponent of intermolecular potential are shown to be related to the microscopic Gruneisen parameter and Beyer's nonlinearity parameter of the liquid. The intermolecular contributions to the heat capacity and the adiabatic bulk modulus have been evaluated from the relationship between the microscopic and thermodynamic Gruneisen parameter, using thermo - acoustic data. The results have been used to develop further understanding of the significance of fractional free volume, repulsive exponent of intermolecular potential and the Gruneisen parameter in describing thermo-acoustic and nonlinear properties and the anharmonic behaviour with regard to molecular order and intermolecular interactions in liquids.

1. INTRODUCTION

Beyer's nonlinearity parameter (B/A) has been expressed [1] in terms of the isobaric acoustical parameter K of Rao and isothermal acoustical parameter K' of Carnevale - Litovitz for liquids. This result presents an improvement over the work of Hartmann [2] and confirms the conclusion on sound propagation data of fluorocarbon fluids and low density solids by Madigosky et al [3] that $(\frac{1}{2}) (B/A)$ is greater than K through the introduction of the isochoric acoustical parameter K'' for a liquid [1]. There is a significant contribution of K'' to the thermo-acoustic and nonlinear properties of liquids [1, 4-6]. The anharmonic microscopic isobaric β , isothermal β' and isochoric β'' Gruneisen parameters are essentially the same [4] as the corresponding acoustical parameters K , K' and K'' for a liquid. The significance of the distinction and the relationship between the microscopic Gruneisen parameter β (as a measure of anharmonicity of normal mode frequency of molecular vibrations) and the conventional thermodynamic Gruneisen parameter $\bar{\beta}$ (used for structural study) of liquids has been discussed [4]. It has been proposed that there are two distinct modes of vibrations, the intermolecular acoustic modes and intramole-

cular optical modes, in quasi-spherical molecular liquids and long chain molecules in which molecular rotation or hindering of neighbouring molecules occurs [7] due to complex thermal motions of molecules. The anharmonic Gruneisen parameter $\bar{\Gamma}$ is determined primarily by the intermolecular vibrations while $\bar{\Gamma}$ is an average overall modes of vibrations, including intermolecular and intramolecular vibrations which employ thermodynamic parameters such as the isochoric C_v and isobaric C_p heat capacities of the liquid.

In this paper, the $\bar{\Gamma}$ ratio ($\bar{\Gamma}/\bar{\Gamma}$) is utilized to measure the contribution of intermolecular vibrations to isobaric heat capacity and adiabatic bulk modulus in quasi-spherical molecular liquids and fluorocarbon fluids. The parameter $\bar{\Gamma}$ is shown to be related to the proportionality factor K_1 for the relation between sound velocity and internal molar latent heat of vaporisation of liquids. Also, the isothermal volume derivatives of C_v and $\bar{\Gamma}$, the repulsive exponent n of intermolecular potential, fractional free (available) volume f (as a measure of disorder due to increased mobility of molecules) are related to the parameters $\bar{\Gamma}'$ and (B/A) through K'' of the liquid. The treatment has the distinct advantage that various parameters describing the anharmonic, nonlinear and thermo-acoustic properties can be evaluated from the thermo-acoustic data of liquids.

2. THEORETICAL

The thermodynamic Gruneisen parameter $\bar{\Gamma}$ and the microscopic Gruneisen parameters $\bar{\Gamma}$ and $\bar{\Gamma}'$ for a liquid [4, 6] can be expressed as

$$\bar{\Gamma} = Li/T C_v = \alpha V B_s / C_p = Li \gamma / T C_p = (\gamma - 1) / \alpha T \quad (1)$$

$$\bar{\Gamma} = -(1/2) [(d \ln B_s / dT)_p / \alpha + 1] = k = -(d \ln C / dT)_p / \alpha \quad (2)$$

$$\bar{\Gamma}' = (1/2) [(d B_s / d p)_T / (\gamma - 1)] = k' = \beta (d \ln C / d p)_T = k + k'' \quad (3)$$

in which the acoustical parameters K'' and K' , using the expressions obtained [1, 6] for the nonlinearity parameter (B/A) and proportionality factor K_1 , may be expressed in terms of (B/A) , r , k , $\bar{\Gamma}$ and K_1 for a liquid as

$$k'' = [(1/2)(B/A) - k] / \gamma = [(1/2)(B/A) - k'] / (\gamma - 1) = [(1/2)(B/A) - k'] / \gamma \bar{\Gamma} K_1 \quad (4)$$

$$k' = k [1 - (B/\gamma)] + (1/2 \gamma)(B/A) = (1/2)(B/A)(1 - \bar{\Gamma} K_1) + k \bar{\Gamma} K_1 \quad (5)$$

$$K_1 = Li / M c^2 = \bar{\Gamma} T C_v / M c^2 = \alpha T / \gamma = (\gamma - 1) / \gamma \bar{\Gamma} \quad (6)$$

$$\gamma = C_p / C_v = B_s / B = 1 + T \alpha^2 M c^2 / C_p = 1 + T \alpha^2 V B_s / C_p = 1 + \bar{\Gamma} \alpha T \quad (7)$$

where M is the molecular weight, Li is the internal molar latent heat of vaporisation, B , B_s , C , V , r and α are respectively the isothermal and adiabatic bulk modulus, sound velocity, molar volume, heat capacity ratio and volume expansivity of the liquid at absolute temperature T and pressure P .

The analogous expression for the microscopic Gruneisen parameter $\bar{\Gamma}$, using eq. (1) and generalising the suggestions on intermolecular vibration contribution [4] to various quantities can be written as

$$\bar{\Gamma}_i = \bar{\Gamma} = Li_i / T C_{v,i} = \alpha V B_{s,i} / C_{p,i} = Li \gamma_i / T C_{p,i} = (\gamma_i - 1) / \alpha T \quad (8)$$

$$\text{Eqs. (1), (6) - (8) transform into the relations given by } \gamma = B_{s,i} / B = C_v C_{p,i} / C_p C_{v,i} = \gamma_i / \gamma = C_{p,i} / X C_p = (1 + \bar{\Gamma} \alpha T) / (1 + \bar{\Gamma} \alpha_i T) \quad (9)$$

$$Z = C_{p,i} / C_p = (C_{v,i} / C_v) (\gamma_i / \gamma) = X \gamma = (\bar{\Gamma} / \bar{\Gamma}_i) (1 + \gamma \bar{\Gamma} K_1) / (1 + \gamma_i \bar{\Gamma}_i K_1) \quad (10)$$

The fractional free (available) volume f and the repulsive exponent n of the intermolecular potential in a liquid [5, 6], using eqs. (3) and (5), can be expressed in terms of $\bar{\Gamma}'$, (B/A) , $\bar{\Gamma}$ and K_1 as

$$f = (\bar{\Gamma}' + 1)^{-1} = (k + 1 + k'')^{-1} = [1 + k \bar{\Gamma} K_1 + (1/2)(B/A)(1 - \bar{\Gamma} K_1)]^{-1} \quad (11)$$

$$n = 6(\bar{\Gamma}' - 3/2) = 3[(2/f) - 5] = 3[(B/A)(1 - \bar{\Gamma} K_1) + 2k \bar{\Gamma} K_1 - 3] \quad (12)$$

Using eqs. (1), (4) - (6) and (12) the expressions obtained [6] for the isothermal volume derivatives of C_v and $\bar{\Gamma}$ for a liquid may be shown to be related to the parameters $\bar{\Gamma}$, (B/A) , n and K_1 as

$$\gamma' = (d \ln C_v / d \ln V)_T = \bar{\Gamma} (K'' - 1) \alpha T = (\gamma - 1)(K'' - 1) = \gamma \bar{\Gamma} K_1 (K'' - 1) \\ = (1/2)(B/A) + 1 - (k' + \gamma) \quad (13)$$

$$\lambda = -(d \ln \bar{V} / d \ln V)_T = k''(\gamma+1) - \gamma = [(1/2)(B/A) - k](\gamma+1)/\gamma - \gamma$$

$$= [(1/2)(B/A) - k](\gamma+1)/\gamma \bar{V} k_1 - \gamma = (1/2)[(B/A) + 2 + (\gamma/3)] - (2k + \gamma) \quad (14)$$

Eqs. (4), (13) and (14) show that $(1/2)(B/A)$ is greater than both K and K' for a liquid, a fact recognised by Madigosky et al [3], thereby introducing significant contribution of K'' to (B/A) for liquids.

3. RESULTS AND DISCUSSION

Calculated values of the parameters $\bar{V}$, k'' , ρ' , k_1 , ρ , γ , Z , n and λ , using eqs. (1) - (6), (9), (10), (12) and (14) for several liquids are presented in table 1. Necessary experimental data on α , γ , C_p , K and (B/A) are taken from literature [1 - 3]. The intermolecular contributions to C_p range from about 11% to 58% for the liquids. This shows that the volume dependent anharmonic acoustic modes represent only 11% to 58% of the normal mode of vibrations that contribute to C_p , thereby giving evidence for exhibiting molecular rotation, in these liquids. The remaining modes are not acoustic in character but are associated with intramolecular modes of vibration. The factor γ has a significant, temperature dependent contribution

Table 1: Anharmonic parameters and intermolecular heat capacity

Liquid	T (K)	k_1	k''	$\bar{V}$	ρ	γ	Z	n	λ
Benzene	303	0.26	0.90	1.14	3.00	1.48	0.56	14.4	0.8
Chlorobenzene	30.3	0.20	1.00	1.06	3.30	1.41	0.45	16.8	1.0
Acetone	303	0.31	1.30	0.83	2.80	1.59	0.47	15.6	1.7
Methyl alcohol	303	0.31	2.00	0.57	2.40	1.58	0.38	17.4	3.2
Freon C 51 - 12	273	0.32	0.37	0.29	6.10	2.87	0.14	29.8	0.3
	293	0.36	1.84	0.23	4.20	2.42	0.13	27.2	2.8
Freon 114 B - 2	273	0.29	2.74	0.89	2.00	1.33	0.58	19.4	5.1
	293	0.32	1.43	0.77	3.00	1.72	0.45	17.6	2.0
Fluorocarbon 43	273	0.22	2.06	0.28	4.60	1.96	0.12	31.0	3.2
	293	0.25	2.57	0.24	3.70	1.87	0.11	28.6	4.2
Fluorocarbon 75	273	0.30	2.34	0.32	3.80	2.05	0.17	27.8	3.8
	293	0.33	2.45	0.27	3.40	2.06	0.16	26.1	4.0
Fluorolube	273	0.23	3.36	0.51	2.30	1.41	0.31	25.0	6.0
	293	0.25	1.94	0.47	3.30	1.72	0.24	22.4	3.0

from about 1.3 to 2.9 to the adiabatic bulk modulus. Eq.(5) imparts a value of (K/K') which varies from about 0.4 to 0.9 as compared to unity as suggested by Nomoto [8] and Hartmann [2] for liquids. The values of the parameter K_1 increase linearly with temperature and range from about 0.20 to 0.36, a trend similar to that observed in fluid hydrogen isotopes [9] and other liquids [6]. Most of the calculated values of the parameter λ vary from about 2 to 5 in these liquids and are positive, suggesting that $\bar{V}$ decreases with volume in liquids. However, the calculated values of the repulsive component n vary from about 14 to 31 as compared to the range from about 11 to 19 for other liquids [6, 10] and from about 16 to 56 for polymers [5]. Higher values of (B/A) , n and ρ' and smaller value of f for fluorocarbon 43 as compared to other liquids show its anharmonic behaviour with strong molecular interactions which is stronger than other

liquids [6, 10] and polymers [5]. The results establish the importance of K'' which contributes significantly to the thermo-acoustic and nonlinear properties of these liquids.

The present treatment offers a convenient means for establishing relationship between the thermo-acoustic, anharmonic and nonlinear properties of liquids and correlating with repulsive exponent and the Gruneisen parameter for liquids.

4. REFERENCES

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