

Liquid fluorine properties by the hardsphere model with attractive interactions

B K SHARMA

Department of Physics, Regional College of Education, Bhubaneswar 751 007, India

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Abstract. We test the validity of an approximate equation of state of real fluids and the expression for surface tension of hardsphere liquids with attractive interactions derived by Sharma and others by obtaining expressions for isothermal compressibility, C_1 -parameter and acoustical parameter and relate them to microscopic Grüneisen parameter. The calculated values for liquid fluorine show fair agreement with experimental values.

Keywords. Fluorine; surface tension; microscopic Grüneisen parameter; characteristic molar volume; hardsphere.

1. Introduction

Bhatnagar and Sharma (1975) obtained an equation of state of real fluids which has successfully been used to obtain various molecular thermodynamic and viscous flow properties of liquids (Bhatnagar and Sharma 1976, Sharma 1976, 1977, 1980a) and surface tension of hardsphere liquids with attractive interactions at the point of contact (Sharma *et al* 1978). Ree *et al* (1964) and Lu *et al* (1967) applied significant structure theory to surface tension of liquids. The concept of translational (external) degrees of freedom ($3C^*$) associated with a molecule of a liquid along the cartesian axes in three dimensions introduced earlier by Bhatnagar and Sharma (1975, 1976), Prigogine (1957) and Flory *et al* (1964), Fang and Wiehe (1973), Renon *et al* (1967, 1968) and Winnick and Prausnitz (1971) and Winnick (1972) is important to achieve better representation of equation of state and satisfactory description of liquid state properties. In a recent paper (Sharma 1979) this concept was used to obtain expressions for frequency of vibration (ν) for a molecule and hence microscopic (lattice) Grüneisen parameter (Γ). It was shown that Γ is not a constant but sensitive to volume and temperature changes. The pseudo-Grüneisen parameter (Γ_G) introduced by Knopoff and Shapiro (1970) characterises the liquid lattice behaviour by taking into account the internal structure, clustering phenomenon and ordering of molecules in liquid state.

Recently Warfield (1974) pointed out that Grüneisen parameter can be determined either from anharmonicity of lattice vibrations or thermodynamic considerations. Hence calculations governed by these lattice vibrations determine Γ while calculations employing thermodynamic parameters (such as the specific heat) give Γ_G . Much confusion has existed in the literature by the failure to recognise the difference between Γ and Γ_G . Slater (1939) showed that $\Gamma \approx \Gamma_G$ holds true for metals and

ionic crystals. No significant attempts have so far been made to relate the Grüneisen parameters to the surface tension (S) of liquids.

In this paper, we have attempted at obtaining expressions for isothermal compressibility (β), pressure coefficient of bulk modulus (C_1) and acoustical parameter (K) from surface tension of hard sphere liquids with attractive interactions (Sharma *et al* 1978) and relate them to Γ (Sharma 1979). We test the validity of these expressions and examine the relationship between Γ and Γ_G and report the results of calculations for liquid fluorine. We also compare our calculated values of S and Γ with the calculations of Ree *et al* (1964), Lu *et al* (1967) and Pandey *et al* (1976) based on the calculated data on thermodynamic properties of Thomson *et al* (1963) using significant liquid structure.

2. Microscopic and pseudo-Grüneisen parameters and surface tension

Using the concept of external degrees of freedom of a molecule of the liquid, Sharma (1979) obtained an expression for Γ as

$$\Gamma = -(\partial \ln v) / \partial \ln V = c^*(\delta/3), \quad (1)$$

$$\text{in which } \delta = \tilde{V}^{1/3} / (\tilde{V}^{1/3} - 1), \quad (2)$$

where $\tilde{V} = (V/V^*)$ is the reduced molar volume and V the molar volume at absolute temperature T , V^* is the characteristic (or hard core) molar volume at absolute zero temperature.

Fang and Wiehe (1973) suggested that V^* of any liquid (or molecule) may be expressed in terms of critical volume $(V_c)_0$ of argon as

$$V^* = V_c(V^*/V_c)_0, \quad (3)$$

where V^* and V_c outside the bracket refer to the given molecule and parameters inside the bracket $(V^*/V_c)_0$ refer to the liquid argon.

Bhatnagar and Sharma (1975) assumed that V^* of a liquid bears a certain ratio to its critical volume (V_c) as

$$V^* = aV_c, \quad (4)$$

where a is the critical state compressibility factor of the liquid.

Sharma (1980a, b) using equations (3) and (4) has given an empirical relation for V^* , and Bhatnagar and Sharma (1975) have given a relation to define C^* as

$$V^* = a_0V_c, \quad (5)$$

$$C^* = 6a[(1 - a_0^{1/3})^2 / (3 - 4a_0^{1/3})], \quad (6)$$

where $a_0 = (V^*/V_c)_0$ is the critical state compressibility factor of argon and the characteristic parameters (starred quantities) C^* and V^* are characteristic of the

substance, independent of temperature and volume (Bhatnagar and Sharma 1975). The pseudo-Grüneisen parameter (Knopoff and Shapiro 1970) characterising the lattice behaviour is usually expressed by the Mie-Grüneisen (1926) equation of state as

$$\Gamma_G = \alpha V / \beta C_v = (\gamma - 1) / \alpha T, \quad (7)$$

where α , C_v and γ are respectively, the thermal expansion coefficient, heat capacity at constant volume and heat capacity ratio of the liquid.

Expressing total pressure (P) of the liquid as the sum of external pressure (p) and internal pressure (p_i), the reduced equation of state of the liquid (Bhatnagar and Sharma 1975) as given by Sharma *et al* (1978) is

$$PV / RT = C^* \delta, \quad (8)$$

where R is the universal gas constant. Equation (8) can be expressed in terms of Γ using equation (1) as

$$PV / RT = 3\Gamma. \quad (9)$$

By taking (8) as the equation of state of real fluids, the expression of Sharma *et al* (1978) for surface tension of a hard sphere liquid with attractive interactions, in contact with its own vapour of negligible density, in terms of (1) becomes

$$S = (3\sigma^* RT / 16V) (3\Gamma - 1), \quad (10)$$

where σ^* is the rigid core molecular diameter.

Equation (10) establishes a relation between S and Γ . Using (1), (2), (5), (6) and (10) we have evaluated the parameters Γ , δ , V^* , C^* and S for liquid fluorine. The necessary experimental data on a , a_0 , σ^* , V and V_c needed for such calculations are taken from (Lange 1967; Hirschfelder *et al* 1954, Hu *et al* 1954; Cady and Hildebrand 1930). The results are presented in table 1.

Table 1. Calculated values of microscopic Grüneisen parameter, pseudo-Grüneisen parameter and surface tension of liquid fluorine (σ^* , Å = 3.653^a; V^* cc mol⁻¹ = 19.40; C^* mol⁻¹ = 0.573).

T (K)	$V^{b,c}$ (cc mol ⁻¹)	δ	Γ Calc	Γ_G Calc ^c	$S \times 10^{-8}$ Nm ⁻¹			
					Expt ^d	Calc.	Calc. ^e	Calc. ^f
55	22.43	20.99	4.010	4.103	—	15.40	—	—
60	22.81	19.19	3.665	3.588	14.2	14.97	15.8	9.43
65	23.13	17.67	3.375	3.210	13.3	14.60	15.0	9.29
70	23.58	15.92	3.042	2.874	12.2	13.74	14.4	8.75
75	23.97	14.70	2.808	2.614	11.6	13.23	13.85	8.32
80	24.38	13.66	2.609	2.364	10.8	12.76	13.1	7.70
85	25.29	11.87	2.268	—	9.85	11.11	12.5	7.25

^aHirschfelder *et al* (1954); ^bHu *et al* (1954); ^cPandey *et al* (1976); ^dKanda (1937); ^eRee *et al* (1964); ^fLu *et al* (1967).

Pandey *et al* (1976) reported the calculations of Γ_G of liquid fluorine at various temperatures, using equation (7) from the data of Thomson *et al* (1963). The calculated values of Γ_G by Pandey *et al* (1976) and experimental values of S by Kanda (1937) along with calculated values of Ree *et al* (1964) and Lu *et al* (1967) are also given in table 1 for comparison with our calculated values of Γ and S using equation (1) and (10).

3. C_1 -parameter and acoustical parameter K

The C_1 parameter serves as a severe test of the equation of state of liquids. Introducing the concept of external degrees of freedom, the modified expression for C_1 -parameter (Moelwyn-Hughes 1951) may be written as (Sharma 1980c)

$$C^* \left[\frac{\partial (1/\beta)}{\partial p} \right]_T = - \left(\frac{C^*}{\beta} \right) \left(\frac{\partial \ln \beta}{\partial p} \right)_T = C^* \left(\frac{\partial \ln \beta}{\partial \ln V} \right)_T, \quad (11)$$

where the subscript T refers to the condition of constant temperature.

It is also of interest to determine an important acoustical parameter K of liquids (Rao 1940, 1941) which is expressed as the ratio of the temperature coefficient of the ultrasonic velocity (U) to the thermal expansion coefficient (α). For a liquid consisting of a mole of molecules and introducing the concept of external degrees of freedom, the modified expression for U in a given direction can be written as (Sharma 1979)

$$U = (\gamma V / M \beta) C^{*/2}, \quad (12)$$

where M is the molecular weight of the liquid.

Assuming to the first approximation that γ does not vary with volume (Gopala Rao and Rao 1966; Sharma 1979), we can easily show by using (11) and (12), that

$$K = -(\partial \ln V) / (\partial \ln V)_T = (C_1 - C^*) / 2. \quad (13)$$

Equation (13) resembles that proposed by Gopala Rao and Rao (1966). However, it differs from their expression through the introduction of the parameter C^* , whereby application to liquids comprising non-spherical and unsymmetrical molecules is made possible (Flory and Abe 1965, Sharma 1979). These differences vanish of course for $C^* = 1$. The values of parameter C^* differ from unity although these may be close to unity for most substances (Fang and Wiehe 1973; Sharma 1977, 1979; Flory *et al* 1964; Flory and Abe 1965; Winnick and Prausnitz 1971; Winnick 1972). Further (13) is identical with that proposed by Sharma (1979) if the present (11) is used to define the C_1 -parameter. However, the present one is a modification and an improvement of the previous work by Sharma (1979) and Moelwyn-Hughes (1951).

Recently, Sharma (1977, 1980d) obtained an expression for thermal pressure coefficient (γ_p) from the reduced equation of state for liquids (Bhatnagar and Sharma 1975) which using equation (1) can be written as (Sharma 1980d)

$$(\alpha/\beta) = (C^* R \delta / V) = (3 \Gamma R / V), \quad (14)$$

where the thermal expansion coefficient α is given by (Sharma 1977)

$$3(\tilde{V}^{1/3} - 1)/[T(4 - 3\tilde{V}^{1/3})]. \quad (15)$$

Using equations (1), (10) and (14) we may write

$$S = (3\sigma^*T/16) [(\alpha/\beta) - (R/V)]. \quad (16)$$

Differentiating (16) with respect to pressure at constant temperature and using (11) we may write

$$(\partial S/\partial p)_T = (3\sigma^*T/16) [(\alpha C_1/C^*) + \beta^{-1} (\partial\alpha/\partial p)_T - (R\beta/V)]. \quad (17)$$

Using (14) and (15) we obtain

$$(\beta R/V) = \alpha/(3\Gamma), \quad (18)$$

$$(\partial\alpha/\partial p)_T = -4\alpha\beta(1 + \alpha T)/3. \quad (19)$$

It was shown by Gopala Rao (1965) for rigid sphere liquids with attractive interactions

$$(\partial S/\partial p)_T = (\sigma^*/4). \quad (20)$$

Equations (17) to (20) lead to the expression for C_1 -parameter as

$$C^*[(3\Gamma)^{-1} + (4/3)(\alpha T)^{-1} + (4/3)(1 + \alpha T)]. \quad (21)$$

Equations (10), (13), (16), (18) and (21) establish inter-relationships amongst S , K , β and C_1 parameter through Γ and α of the liquid. Using (21) and (13) we have evaluated the C_1 -parameter and K for liquid fluorine at various temperatures. The α values needed for our calculations are taken from Thomson *et al* (1963). The calculated values of C^* and Γ are taken from table 1. The results are presented in table 2.

Table 2. Calculated values of C_1 -parameter and acoustical parameter K of liquid fluorine. ($C^* \text{ mol}^{-1} = 0.573$).

T (K)	Γ	$\alpha \times 10^{3\alpha}$ (K ⁻¹)	C_1	K
60	3.665	3.118	5.511	2.469
65	3.375	3.259	4.591	2.090
70	3.042	3.540	4.100	1.764
75	2.808	3.784	3.741	1.584
80	2.609	4.098	3.418	1.422

^aThomson *et al* (1963).

4. Results and discussion

The calculated values of Γ and S using (1) and (10) over the temperature range from 55K to 85K given in table 1 show fair agreement with respective calculations for Γ_G using equation (7) (Pandey *et al* 1976; Kanda 1937). These parameters are temperature-dependent and continuously decrease with increase of temperature in accordance with experiment. It may be observed that our calculated values of S using (10) show better agreement with experiment as compared to those calculated by Ree *et al* (1964) and Lu *et al* (1967). Further, the calculated values of Γ and Γ_G are very close so that their ratio is very close to unity. This suggests that the relationship $(\Gamma/\Gamma_G) \approx 1$ for metals and ionic crystals (Slater 1939), liquid mercury (Sharma 1980e) and simple liquefied gases (Sharma 1979) also holds true for liquid fluorine.

The present calculations given in table 2 for C_1 -parameter and acoustical parameter K using (21) and (13) for liquid fluorine in the temperature range from 60K to 80K are found to be reasonably good. Since experimental values of these parameters are not available for liquid fluorine, no comparison could be made. However, the present values show a satisfactory agreement with the values of C_1 -parameter and acoustical constant K respectively, around 5 or 6, and 2, as reported by Sharma (1979), Aziz *et al* (1972) and Gopala Rao and Joardar (1976) for liquefied gases and non-ionic simple liquids. The calculated values of C_1 -parameter show a decrease from about 5.51 to 3.42 and those of acoustical parameter K from 2.47 to 1.42 as the temperature is raised from 60K to 80K. This behaviour is similar to that of both Γ and Γ_G . The evaluation of C_1 -parameter forms a severe test of the equation of state. The reasonably satisfactory values of the present calculations for C_1 -parameter and the acoustical parameter K provide an additional support to the equation of state proposed by Sharma *et al* (1978).

We have given formulae for estimating, S , C_1 -parameter and K in terms of the parameters C^* , Γ and α of the liquid. These have been derived by applying hard sphere concepts, with attractive interactions through (8) for equation of state and (20) for the pressure coefficient of the surface tension. It was shown by several workers (Yosim and Owens 1963; Yosim 1964; Mayer 1963; Gopala Rao 1965, 1975; Gopala Rao and Murthy 1973; Gopala Rao and Shyamasunder 1974; Gopala Rao and Nammalvar 1975; Gopala Rao and Joardar 1976; Sharma *et al* 1978; Sharma 1980f) that the hard sphere concept and equation (20) can be applied extensively for deriving various thermodynamic, transport, acoustical and other bulk properties related to surface tension of realistic liquids. They have concluded that the simple non-polar and slightly polarisable molecules give reasonably good values, thereby showing that these molecules can be represented by rigid spheres. The present results confirm these conclusions and show that liquid fluorine can be described satisfactorily by rigid sphere model with attractive interactions.

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References

- Aziz R A, Bowman D H and Lim C C 1972 *Can. J. Phys.* **50** 646
- Bhatnagar H L and Sharma B K 1975 *Indian J. Pure Appl. Phys.* **13** 328
- Bhatnagar H L and Sharma B K 1976 *Indian J. Pure Appl. Phys.* **14** 107
- Cady G H and Hildebrand J H 1930 *J. Am. Chem. Soc.* **52** 3839
- Fang H H and Wiehe I A 1973 *Ind. Eng. Chem. Fundam.* **12** 173
- Flory P J, Orwoll R A and Vrij A 1964 *J. Am. Chem. Soc.* **86** 3507 3515
- Flory P J and Abe A 1965 *J. Am. Chem. Soc.* **87** 1833 1838
- Gopala Rao R V 1965 *Indian J. Pure Appl. Phys.* **3** 233
- Gopala Rao R V and Rao B S M 1966 *Trans. Faraday Soc.* **62** 2704
- Gopala Rao R V and Murthy A K 1973 *Z. Phys. Chem. Neue Folge* **86** 75
- Gopala Rao R V and Shyamasunder K V S 1974 *Indian J. Phys.* **48** 236
- Gopala Rao R V 1975 *Indian J. Pure Appl. Phys.* **13** 459
- Gopala Rao R V and Joardar R N 1976 *Indian J. Pure Appl. Phys.* **14** 905
- Gopala Rao R V and Nammalvar T 1975 *Acustica* **33** 127; **34** 38
- Grüneisen E 1926 *Handb. Phys.* **10** 21
- Hirschfelder J O, Curtis C F and Bird R B 1954 *Molecular theory of gases and liquids* (New York : John Wiley)
- Hu J H, White D and Johnston H L 1954 *J. Am. Chem. Soc.* **76** 2584
- Kanda E 1937 *Bull. Chem. Soc. Jpn.* **12** 469
- Knopoff L and Shapiro J N 1970 *Phys. Rev.* **B1** 3893
- Lange N A 1967 *Handbook of Chemistry* (New York: McGraw Hill) p. 1669
- Lu W C, John M S, Ree T and Eyring H 1967 *J. Chem. Phys.* **46** 1075
- Mayer S W 1963 *J. Phys. Chem.* **67** 2160
- Moelwyn-Hughes E A 1951 *J. Phys. Chem.* **55** 1246
- Pandey J D, Bhatt T and Pant U R 1976 *Indian J. Pure Appl. Phys.* **14** 410
- Prigogine I 1957 *Molecular theory of solutions* (Amsterdam: North Holland)
- Rao M R 1940 *Indian J. Phys.* **14** 109
- Rao M R 1941 *J. Chem. Phys.* **9** 682
- Ree T S, Ree T and Eyring H 1964 *J. Chem. Phys.* **41** 524
- Renon H, Eckert C A and Prausnitz J M 1967 *Ind. Eng. Chem. Fundam.* **6** 52
- Renon H, Eckert C A and Prausnitz J M 1968 *Ind. Eng. Chem. Fundam.* **7** 335
- Sharma B K 1976 *Indian J. Pure Appl. Phys.* **14** 939, 992
- Sharma B K 1977 *Indian J. Pure Appl. Phys.* **15** 633
- Sharma B K 1979 *Acustica* **43** 221
- Sharma B K 1980a *Indian J. Phys.* **53B** 474
- Sharma B K 1980b *Acustica* **44** part 2 (to appear)
- Sharma B K 1980c *Phys. Status Solidi (B)* **99**, Part 2
- Sharma B K 1980d *Acustica* **44** Part 1, 3 (to appear)
- Sharma B K 1980e *Indian J. Pure Appl. Phys.* (to appear)
- Sharma B K 1980f *Indian J. Pure Appl. Phys.* **18** 457
- Sharma B K, Chandrasekhar M A and Kumar S 1978 *Indian J. Pure Appl. Phys.* **16** 1068
- Slater J C 1939 *Introduction to chemical physics* (New York: McGraw Hill) p. 238
- Thomson T R, Eyring H and Ree T 1963 *J. Phys. Chem.* **67** 2701
- Warfield R W 1974 *Makromol. Chem.* **175** 3285
- Winnick J and Prausnitz J M 1971 *Chem. Eng. J.* **2** 233
- Winnick J 1972 *Ind. Eng. Chem. Fundam.* **11** 239
- Yosim S J 1964 *J. Chem. Phys.* **40** 3069
- Yosim S J and Owens B B 1963 *J. Chem. Phys.* **39** 2222