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Velocity of sound and an equation of state for liquids

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An expression for the total pressure of liquids from the concept of sound propagation through liquids was derived. The equation connects the total pressure of the liquid to the molecular diameter d and a dimensionless parameter δ. The calculated values of the molecular diameter d agree well with those obtained by other methods. To test the validity of the pressure equation, the compressibilities and the pressure variation of bulk modulus were derived and compared with experimental value and it was found to give satisfactory agreement. It is shown that the total pressure, P, varies in a linear way with $1/\beta_T$, the isothermal bulk modulus. It was found that the attractive pressure can be better expressed as aV^{-n} and not as aV^{-2}, as in the case of Van der Waals equation especially in the liquid state of the fluid. In general, it was found that the value of n is around 2 and not exactly 2, the average value being 1.91.

Introduction

Sound propagation in a fluid is a very important illustration of compressional wave motion in a material medium. The propagation of acoustic disturbance is connected with intermolecular forces since the disturbance while being propagated has to overcome the internal forces of attraction. In the case of the gaseous phase of the fluid the forces of attraction are weak while strong forces of attraction and repulsion dominate in the liquid phase of the fluid. Hence sound velocity has to be considered as a primary property of liquids in a molecular kinetic theory and not a secondary property derived from compressibility as in normal thermodynamics.

Equation of state from sound velocity

As is well known the velocity of sound is given by (Hirschfelder 1954)

$$C^3 = (V/V_f)(\gamma RT/M)^{3/2} \qquad \ldots(1)$$

where, C = velocity of the sound in fluids, V = molar volume of the liquid, and V_f = molar free volume. The rest of the symbols have their usual connotation.

If a compressional wave is propagated through fluid it is easy to show that (Lindsay 1960 ; Blitz 1963),

$$C^2 = (dP/d\rho)_S = \gamma\,(dP/d\rho)_T \qquad \ldots(2)$$

From equations (1) and (2) we get

$$(dP/dV)_T = -(RT/V_f^{2/3})(1/V^{4/3}) \qquad \ldots(3)$$

Along with others we assume that the molar free volume of fluids is given by (Eyring 1937 ; Hirschfelder 1954)

$$V_f = b^3 (V^{1/3} - N^{1/3}d)^3 \qquad ...(4)$$

where b is a constant depending upon the type of packing ($b = 2$, 1.835 & 1.78 for SCC, BCC. & FCC respectively) and d is the so called incompressible diameter of the molecule. In case of gases $V_f = V$, since $N^{1/3} d$ is negligible and b is unity.

From (3) and (4), we get

$$dP = -\frac{RTdV}{b^2 (V^{1/3} - N^{1/3}d)^2 V^{4/3}} \qquad ...(5)$$

$$P = \frac{3\,RT}{b^2 A^3}\left[\frac{X}{X-A} + \frac{A}{X} - 1 + 2\,ln\left(\frac{X-A}{X}\right)\right] + K_1(T) \qquad ...(6)$$

where, $A = N^{1/3}d$, $X = V^{1/3}$, and $K_1(T)$ = a constant of integration and is independent of volume.

Thus, we have an equation of state for fluids. To evaluate the integration constant $K_1(T)$ we use the well known Maxwell theorem (De Boer 1964)

$$\int_{V_l}^{V_g} P.\,dV = P\,(V_g - V_l) \qquad ...(7)$$

If we are very much below the critical temperature which is true at room temperatures, we have $V_g \gg V_l$. Further assuming that at these low vapour pressures ($\sim$ 0.1 atm.) we can safely assume that the vapour is ideal. Hence, we have from equation (7)

$$\int_{V_l}^{V_g} P.\,dV = RT \qquad ..(8)$$

Using equations (6) and (8), we get

$$RT = \int_{x_l}^{x_g} \frac{9RT}{b^2A^3}\left[\frac{x}{x-A} + \frac{A}{x} - 1 + 2\,ln\left(\frac{x-A}{x}\right)\right] x^2dx + \int K_1(T).dV \qquad ...(9)$$

where, $x_l = V_l^{1/3}$ and $x_g = V_g^{1/3}$.

After lengthy but straightforward integration, we obtain the value of $K_1(T)$ to be

$$K_1(T) = \frac{RT}{(x_g^3 - x_l^3)} - \frac{3RT}{b^3A^3(x_g^3 - x_l^3)}\Big\{2A(x_g^3 - x_l^2) + A^2(x_g - x_l)$$

$$+ A^3 \ln\left(\frac{x_g - A}{x_l - A}\right) + 2x_g^3 \ln\left(\frac{x_g - A}{x_g}\right)$$

$$- 2x_l^3 . \ln\left(\frac{x_l - A}{x_l}\right)\Big\} \qquad \ldots(10)$$

from which we write after transformation into V_g and V_l

$$P = \frac{3RT}{b^2Nd^3}\Bigg[\frac{V_l^{1/3}}{V_l^{1/3} - N^{1/3}d} - \frac{V_l^{1/3} - N^{1/3}d}{V_l^{1/3}} + 2\ln\left(\frac{V_l^{1/3} - N^{1/3}d}{V_l^{1/3}}\right)$$

$$+ \frac{b^2Nd^3}{3(V_g - V_l)} - \frac{1}{(V_g - V_l)}\Big\{2N^{1/3}d\left(V_g^{2/3} - V_l^{2/3}\right)$$

$$+ N^{1/3}d^2\left(V_g^{1/3} - V_l^{1/3}\right) + Nd^3 \ln\left(\frac{V_g^{1/3} - N^{1/3}d}{V_l^{1/3} - N^{1/3}d}\right)$$

$$+ 2V_g \ln\left(\frac{V_g^{1/3} - N^{1/3}d}{V_g^{1/3}}\right) - 2V_l \ln\left(\frac{V_l^{1/3} - N^{1/3}d}{V_l^{1/3}}\right)\Big\}\Bigg] \qquad \ldots(11)$$

If we are far below the critical temperature $V_g \gg V_l$ and hence $V_{l_g}^{1/3} \gg V_l^{1/3}$, then the above equation (11) can be reduced to

$$P = \frac{3RT}{b^2Nd^3}\left[\frac{V_l^{1/3}}{V_l^{1/3} - N^{1/3}d} - \frac{V_l^{1/3} - N^{1/3}d}{V_l^{1/3}} + 2\ln\left\{\frac{V_l^{1/3} - N^{1/3}d}{V_l^{1/3}}\right\}\right] \qquad \ldots(12)$$

In this connection it is found out that the contribution due to the term $b^2Nd^3/3(V_g - V_l)$ is also negligible since Nd^3 itself is less than V_l.

We define now a dimensionless parameter (Gopala Rao 1967)

$$\delta \equiv \frac{3C_1 - 1}{2} \qquad \ldots(13)$$

and it was shown that

$$\delta = \frac{V_l^{1/3}}{V_l^{1/3} - N^{1/3}d} \qquad \ldots(14)$$

From equations (12) and (14) we get

$$P = \frac{3RT}{b^2Nd^3}\left[\delta - \frac{1}{\delta} - 2\ln\delta\right] \qquad \ldots(15)$$

Equations (12) and (15) are surprisingly simple and are important since they give a valuable method for the evaluation of compressibilities and other thermodynamic properties of liquids. Further (12) and (15), even though derived from velocity consideration does not contain a term involving velocity through liquids. Further equation (12) and (15) connect the pressure to a microscopic property d, the molecular diameter.

Here the pressure is the total pressure and is the sum of kinetic and static pressures, sometimes referred to as the internal pressure. It can be shown from thermodynamics that (Moelwyn-Hughes 1961)

$$P = T\,(dP/dT)_V - (dE/dV)_T \qquad ...(16)$$

Total pressure = Kinetic pressure + Static pressure.

The kinetic pressure is due to thermal motion and is always positive while the static pressure may be positive, negative or zero. It can be shown from elementary thermodynamics that

$$P_k = T\,(dP/dT)_V = \alpha_T/\beta_T \qquad ...(17)$$

and $P_s = -(dE/dV)_T$ ...(18)

Hence $P = \dfrac{\alpha_T}{\beta_T} - \dfrac{a}{V^2}$.

Comparing it with Van der Waals equation we have

$$P_s = -\frac{a}{V^2} \qquad ...(19)$$

Hence we have from (15), (17), (18) and (19)

$$P = \frac{\alpha_T}{\beta_T} - \frac{a}{V^2} = \frac{3RT}{Nb^2d^3}\left[\delta - \frac{1}{\delta} - 2\ln\delta\right] \qquad ...(20)$$

The molecular diameters were calculated from equation (20). The values so calculated are given in table 1 for various types of packing. The d values so calculated agree well with those obtained by other methods (Hirschfelder 1954 ; Handbook of Chemistry and Physics 1958 ; Gopala Rao 1969).

A further test of equation (15) is the evaluation of compressibility coefficients of the liquids. Remembering that

$$\beta_T = -\frac{1}{V}\left(\partial V/\partial P\right)_T$$

we obtain from equation (15) that

$$\frac{1}{\beta_T} = -\frac{RT}{b^2Nd^3}\left[\frac{b^2V^{1/3}}{V_f^{\,2/3}}\left(\frac{2V_f^{\,1/3}}{b} - N^{1/3}d\right) - \frac{N^{1/3}d}{V^{1/3}} - 2 + \frac{1}{V_g}\left\{\frac{bV^{1/3}}{V_f^{\,1/3}}Nd^3 + 6V\ln\left(\frac{V_f^{\,1/3}}{V^{1/3}b}\right) + \frac{2bVN^{1/3}d}{V_f^{\,1/3}}\right\}\right] \qquad ...(21)$$

On omitting certain negligible terms we get,

$$\frac{1}{\beta_T} = \frac{RT}{b^2 N d^3}\left[\frac{N^{1/3}d}{V^{1/3}}\left\{\delta^2 + 1\right\} + 2 - 2\delta\right] \qquad \ldots(22)$$

Equation (22) is very simple and is important since β_T is directly connected with the liquid parametet δ and molecular diameter d. The compressibility coefficients were evaluated for some thirteen liquids (for FCC type of packing only) and compared with the experimental values. The results are given in table 1 and the agreement is found to be very good.

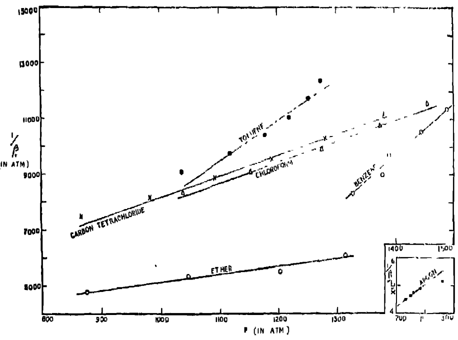

Figure 1

Remembering that (equation 14)

$$\frac{V^{1/3} - N^{1/3}d}{V^{1/3}} = \frac{1}{\delta}$$

we can rewrite equation (22) as

$$\frac{1}{\beta_T} = \frac{RT}{Nb^2d^3}\left[(\delta - 4)(\delta + 1) + 7\right] \qquad \ldots(23)$$

One can therefore use the experimental compressibility coefficients and then calculate the molecular diameters d from the above equation.

Dividing equation (20) by (23) and rearranging we get

$$P = \frac{1}{\beta_T} \cdot \frac{3\left[\delta - \frac{1}{\delta} - 2\ln\delta\right]}{\left[(\delta - 4)(\delta + 1) + 7\right]} \qquad \ldots(24)$$

TABLE—1.

Sl. No.	Substance	Temp. (T) (°Abs.)	δ	κ (× 10⁻²)	a [lit.² atm./mole²]	V [c.c./mole]	p (atm.)	d (A°)(From Eq. 20) SCC b=2. 000	BCC b=1. 835	FCC b=1. 780	b (A°) (other data) (Viscosity)	(Rigid sphere)	(Critical)	C_1 From Eq. (25)	C_1 (Exptl.)	$\frac{\beta \times 10^6}{T}$ From Eq. (22) (FCC only atm⁻¹	$\frac{\beta \times 10^6}{T}$ (Exptl.) (atm⁻¹	n From Eq. (26)
(a)	*Hydrocarbons :*																	
1.	Hexane	296	11.1	1.352	24.39	131	1105	5.53	5.86	5.98	5.910	6.38	5.16	8.45	7.8	157	159	2.12
2.	Octane	296	12.3	1.147	37.32	163	1391	5.40	5.71	5.83	7.450	7.09	5.73	8.40	8.5	—	121	1.95
3.	Benzene	293	11.5	1.209	18.00	89	1445	5.13	5.44	5.55	5.270	5.66	4.51	9.20	8.0	104	95	1.87
4.	Toluene	293	11.5	1.035	24.06	106	1218	5.44	5.76	5.87	—	6.04	4.90	9.18	8.0	99	91	1.74
(b)	*Esters :*																	
5.	Methyl acetate	293	11.5	1.369	15 29	79	1540	5.03	5.33	5.43	—	5.40	4.44	9.35	8.0	73	101	1.94
6.	Ethyl acetate	293	11.5	1.352	20.45	98	1645	4.91	5.20	5.30	—	5.85	4.80	8.50	8.0	91	105	1.96
7.	Ethyl propionate	293	11.5	1.273	24.39	115	1810	4.76	5.05	5.15	—	6.22	5.04	7 81	8.0	105	102	1.98
8.	Ethyl butyrate	293	12.3	1 201	30.07	132	1760	4 97	5.26	5.36	—	6.60	5 34	8.30	8.5	107	101	1.98
(c)	*Miscellaneous :*																	
9.	Ether	283	10.8	1.693	17.38	102	1202	5.25	5.55	5.67	—	5 78	4.74	8.55	7.5	153	167	2.00
10.	Chloroform	293	11.8	1.248	15.17	80	1274	5.42	5.75	5 85	5 430	5.43	4.33	10 60	8.2	100	101	1.83
11.	Acetone	273	9.3	1.425	13 91	73	1560	4.40	4.65	4.75	—	5.06	4.28	7.00	6.5	101	93	1,84
12.	Carbon tetrachloride	293	12.4	1.208	20.39	97	1189	5.69	6.03	6 15	5.881	5 84	4.79	10.60	8.6	112	105	1 88
13.	Ethylene bromide	293	11.6	0.963	13.98	86	2895	4 09	4.33	4.42	—	5 45	4.10	7 43	8 1	65	59	1.91
14.	Carbon disulphide	319	10.8	1.194	11.62	59	1055	5.69	6 03	6.15	4.438	4.60	4.00	—	—	63	87	1.82
15.	Argon	86	9.2	4.470	1.35	29	242	4.48	4 75	4.84	3.400	3 60	2.94	—	—	—	234	1.77

TABLE 2.

Sl. No.	Substance	Temp. (T) (°Abs.)	Density (gm/cc)	V (cc)/Mole	α ($\times 10^{-3}$)	$\beta_T \times 10^6$ (atm^{-1})	$P = \frac{\alpha_T}{\beta_T} - \frac{a}{V^2}$ (atm.)	$\frac{1}{\beta_T}$ (atm.)
1.	Tolune	273	0.8848	104.0	1.035	80.8	1273	12380
		283	0.8752	105.2		85.5	1252	11700
		293	0.8657	106.3		90.6	1218	11040
		303	0.8563	107.5		96.2	1177	10390
		313	0.8470	108.7		102.7	1118	9740
		323	0.8378	109.9		110.4	1036	9091
2.	Chloroform	273	1.5264	78.21	1.248	86.6	1454	11550
		283	1.5078	79.17		93.1	1374	10740
		293	1.4888	80.19		100.7	1274	9901
		303	1 4697	81.23		109.5	1153	9091
		313	1.4505	82.30		119.5	1028	8333
3.	Ether	273	0.7362	100.7	1 693	152.7	1314	6536
		283	0.7248	102.3		167.4	1202	5988
		293	0.7135	103.9		186.8	1046	5348
		303	0.7019	105.6		210.8	875	4739
4.	Carbon tetrachloride	273	1.6327	94.22	1 2076	89.7	1379	11150
		283	1.6134	95.35		97.0	1281	10310
		293	1.5939	96.51		104.8	1189	9524
		303	1.5748	97.68		113.3	1092	8850
		313	1.5557	98.88		123.2	982	8130
		323	1.5361	100.14		134.4	867	7463
5.	Benzene	283	0.8896	87.74	1.190	88.	1488	11360
		293	0.8790	88.79	1.209	95	1445	10530
		303	0.8684	89.88	1.230	103	1390	9709
		313	0.8576	91.01	1.259	111	1377	9009
		323	0.8467	92.18	1.280	120	1327	8333
6.	Argon	84	1.402	28.49	4.45	193	279	5181
		86	1.396	28.61	4.47	204	242	4902
		87	1.390	28.73	4.49	210	230	4762
		88	1.383	28.88	4.51	216	225	4630
		89	1.378	28.99	4.53	222	216	4505

From equation (24) we see that if we plot P versus $1/\beta_T$ we must get a straight line. The necessary data (Freyer 1929 ; Yosim 1964) is presented in table 2 and the plot is given in figure 1. Unfortunately the slopes obtained from the graphs are not in agreement with those calculated from equation (24).

The pressure variation of bulk modulus of liquids is an important quantity as it is related to molecular force constants (Gopala Rao 1962 ; Moelwyn Hughes 1951). Thus we define

$$C_1 = \left[\frac{\partial(1/\beta_T)}{\partial P} \right]_T$$

using equation (23) we get after simplification for C_1 as

$$C_1 = \frac{N^{1/3}d}{V^{1/3}} \cdot \frac{\delta^2 (2\delta - 3)}{3 [(\delta - 4)(\delta + 1) + 7]} \qquad \ldots (25)$$

Using equation (25) the values of C_1 were calculated and were compared with those obtained from experiment. It is very gratifying to find that the agreement is good.

The attractive internal pressure

It may be pointed out that the attractive pressure can be expressed as aV^{-n} and not as aV^{-2} as in the Van der Waals equation. Thus, n may not be exactly equal to 2 as in Van der Waals equation but may be slightly different from it. Thus, from equations (20) and (24), we have

$$\frac{\alpha_T}{\beta_T} - \frac{a}{V^n} = \frac{3\left(\delta - \frac{1}{\delta} - 2 \ln \delta \right)}{\beta_T [(\delta - 4)(\delta + 1) + 7]} \qquad \ldots (26)$$

From a knowledge of α, β_T, δ, a and V it is possible to calculate n. Such calculations are made and given in the last column of table 1. It is observed that the value of n is slightly less than 2 in most of the cases, the average value being 1.91.

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