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SOUND VELOCITY AND VAN DER WAAL'S FORCE IN LIQUIDS*

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ABSTRACT

Theoretical calculations of the sound velocity and Van der Waal's force in liquids according to significant structure theory are carried out.

The excellent agreements between theory and experiment provide another piece of evidence for its general applicability of the model. The technique to evaluate those properties may be useful to understand the some properties and structures of sea water.

The significant structure theory of liquid (1) has been the most widely applied of the various theories of liquids. It has been applied with success to predict the thermodynamic, dielectric, transport and surface properties of many liquid systems ranging from simple liquids such as argon to complicated systems such as water or some mixtures. This model for liquids is based on several confirmed experimental facts. In this regard, the model is the most acceptable one of those offered today (2).

In this paper, we will discuss the further validity of the model by checking the velocities of sound and Van der Waal's forces in liquids. Since these properties are related to the second derivative of the partition function, their results will constitute a severe test of the model. According to the significant structure theory, the partition function of liquids can be expressed as follows,

$$f=f_s^{N\frac{V_s}{V}}\cdot f_g^{N\frac{V-V_s}{V}} \qquad (1)$$

where, f_s is the partition function for the solid-like degree of freedom with positional degeneracy and f_g is the partition function for the gas-like degree of freedom, V and V_s are the molar volumes of the liquid and solid, respectively and N is the number of molecules. In the recent literature (3), one sees that for simple liquids, the model works without any adjustable parameters.

SOUND VELOCITY IN LIQUIDS

According to well known relations, the velocity of sound C obeys the following equation.

$$C=\left[\frac{\gamma}{\beta_T\rho}\right]^{\frac{1}{2}}=\left[\frac{C_P V}{C_V\beta_T M}\right]^{\frac{1}{2}} \qquad (2)$$

where, γ is the ratio of C_P to C_V, β_T is the isothermal compressibility, ρ is the density, V is the molar volume and M is the molecular weight. These quantities may be evaluated in terms of the partition function as follows.

$$\beta_T{}^{-1}=-VkT\left(\frac{\partial^2\ln f}{\partial V^2}\right)_T$$

$$C_V=\left[\frac{\partial}{\partial T}\left\{kT^2\left(\frac{\partial\ln f}{\partial T}\right)_V\right\}\right]_V \qquad (3)$$

$$C_P=C_V+\frac{\alpha^2}{\beta_T}VT \quad \text{here,}$$

$$\alpha=\frac{\left\{\frac{\partial^2(-kT\ln f)}{\partial V\partial T}\right\}_{T,V}}{VkT\left(\frac{\partial^2\ln f}{\partial V^2}\right)_T}$$

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The velocity of sound in several liquids has been calculated and the data are shown in Table 1.

Table 1. Sound velocity of liquid.

	T(°K)	Ccalc (cm/sec)	Cobs (cm/sec)	△%
Ar	84.76	916.7	855.8[a]	7.1
	94.15	816.7	789.9	3.4
	105.31	704.4	707.0	−0.4
	114.94	613.2	629.2	−2.5
	124.09	529.6	546.8	−3.1
	133.11	447.7	454.9	−1.6
Kr	117.0	725.3	700.0[b]	3.6
	132.0	641.5	640.0	0.2
	142.0	586.1	597.0	−1.8
	152.0	532.6	551.0	−3.3
	172.0	429.9	455.0	−5.5
Xe	161.80	676.0	659.0[b]	2.6
	173.00	638.4	623.0	2.5
	203.00	529.4	533.0	−0.7
	223.00	460.2	471.0	−2.3
	243.00	392.9	402.0	−2.3
N_2	65.42	1024.3	968.1[a]	5.8
	70.03	960.9	923.5	4.0
	74.25	901.8	881.4	2.3
	79.34	832.7	830.5	0.3
	84.95	760.3	772.3	−1.6
	110.25	472.3	472.2	0.0
O_2	89.66	959.3	909.9[a]	5.4
	102.23	805.2	804.6	0.1
	113.69	683.1	700.5	−2.5
	131.90	512.1	517.1	−1.0
	140.74	434.9	412.6	5.4
CH_4	90.90	1724.2	1531.0[b]	12.6
	103.60	1533.5	1406.0	9.1
	121.00	1284.5	1236.0	3.9
	133.70	1123.2	1101.0	2.0
	147.40	965.4	954.0	1.2
	168.80	742.8	672.0	10.5
CCl_4	263.15	1080.5	1035.8[c]	4.3
	273.15	1046.8	1003.0	4.4
	283.15	1007.3	969.4	3.9
	293.15	966.5	938.1	3.0
	303.15	926.2	905.9	2.2
$TiCl_4$	273.15	1179.3	1064.2[c]	10.8
	283.15	1133.1	1037.8	9.2
	293.15	1089.2	1009.7	7.9
	303.15	1047.6	982.9	6.6

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VAN DER WAAL'S FORCE IN LIQUIDS

The Van der Waal's constant "a" in liquid can be evaluated from the following relation,

$$\left(\frac{\partial E}{\partial V}\right)_T = kT^2\left(\frac{\partial^2 \ln f}{\partial V \partial T}\right)_{T,V} \tag{4}$$

together with the result derived from Van der Waal's equation and the thermodynamic relation

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$a = V^2\left(\frac{\partial E}{\partial V}\right)_T \tag{5}$$

The value of "a" was calculated for liquid CCl_4 and $TiCl_4$ at various temperatures: The results are shown in Table 2 along with the experimentally observed values at the same temperatures.

Table 2. Van der Waal's constant "a" of liquid.

CCl_4		
T(°K)	a_{calc}(atm × liter^2)	a_{obs}[a*](atm × liter^2)
293.55	28.620	31.18
293.78	28.619	31.23
298.99	28.575	31.18
304.40	28.533	31.23
310.24	28.489	31.22
$TiCl_4$		
T(°K)	a_{calc}(atm × liter^2)	a_{obs}[a*](atm × liter^2)
293.15	38.58	…
294.96	38.53	42.00
298.15	38.45	41.86
300.15	38.40	…
303.15	38.32	41.89

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Data and partition functions used to calculate the velocity of sound and Van der Waal's constant were obtained from the following references; liquid Ar, Kr, Xe and N_2 (3), liquid CCl_4 (4), liquid CH_4 (5), liquid O_2 (6) and liquid $TiCl_4$ (7).

DISCUSSION

The agreement between the calculated values and the experimentally observed values is satisfactory.

The results might be improved by modifying the ideal gas partition function as imperfect one (3) or introducing the hindered rotation in solid-like partition function. The success of significant structure theory in predicting the velocity of sound and Van der Waal's constant "*a*", which are dependent upon the second derivatives of partition function, is another piece of evidence for its general applicability.

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