R & D NOTES

Sound Velocity in Liquid CCl_2F_2 and the Law of Corresponding States

GREGORY R. POOLE and RONALD A. AZIZ

Department of Physics
University of Waterloo, Waterloo, Ontario

At low frequencies and amplitudes, the velocity of sound V in a liquid is a simple thermodynamic property of a substance. Because of the precision with which it can be measured, the velocity of sound is a very suitable property to use in testing the principle of corresponding states (Lim and Aziz, 1966). On the assumption that the principle is valid, one can obtain precise values for the relative parameters of an effective intermolecular potential $\phi = \epsilon F\left(\frac{\sigma}{r}\right)$ proposed for a substance by determining which parameters will "force" corresponding states (Aziz et al., 1967; Lim et al., 1968).

Various sets of ϵ/k and σ of the Lennard-Jones 6-12 potential have appeared in the literature for a single compound. The principle of corresponding states (applied to liquid sound velocity data) may be useful in ascertaining which set of parameters is more valid. The group of interest here includes the roughly spherical molecules CF_4, CCl_2F_2, and CCl_4. Nierode et al. (1970) inferred molecular parameters ϵ and σ by comparing experimental acoustic gaseous velocity data with values of velocity derived on the basis of the equation

$$V^2 = \left(\frac{\partial P}{\partial \rho}\right)_s \qquad (1)$$

with the use of Gyorog-Obert generalized virial equation of state expressed in terms of ϵ and σ. For the gases CF_4 and CCl_2F_2, their values of ϵ/k and σ differ significantly from other values quoted in the literature (Gyorog and Obert, 1964; Hirschfelder et al., 1954) based on an analysis of second virial coefficient data. Agreement between values of the third virial coefficient $C(T)$ based on Douslin's (1964) experimental compressibility measurements and those determined from the Gyorog-Obert equation of state with the new parameters included lend support to the validity of the new parameters. Application of the principle of corresponding states to sound velocity data on liquid CCl_2F_2 presented in this Note and on liquid CF_4 (Aziz et al., 1967) appear to confirm Nierode et al.'s values of ϵ/k for these substances. The assumption is made that the same "effective" intermolecular potentials (Lennard-Jones 6-12) are applicable to both gaseous and liquid phases.

APPARATUS AND METHOD

The velocity of sound was measured in liquid CCl_2F_2 from near its triple point to 198 K with the use of a pulse superposition technique described by Bowman (1967). The gas was supplied by Matheson of Canada Ltd. with a stated purity of 99.0%. There is an uncertainty of about ± 0.2% in the data; this arises mainly from an uncertainty in the determination of the pulse repetition frequency owing to the high attenuation in the liquid at higher temperatures. The temperature was measured with the use of a Tinsley platinum resistance thermometer calibrated at the National Physical Laboratory in England (Barber, 1969).

RESULTS

The data presented in Table 1 were fitted by the method of least squares to the curve

$$V = 1\,858.781\,93 - 4.748\,319\,51\,T \qquad (2)$$

Standard estimate of error = 2.18 m/s

The data are also plotted in Figure 1 as a function of temperature.

Table 1. Velocity of Sound in CCl_2F_2 Under Saturated Vapor Pressure

Temperature, *K.*	Observed velocity, *m/s*	Calculated velocity *m/s*	% deviation from calculated velocity
116.700	1305.8	1304.7	0.08
120.357	1288.0	1287.3	0.05
124.200	1268.7	1269.0	−0.03
130.047	1240.2	1241.3	−0.09
134.555	1217.7	1219.9	−0.18
136.257	1209.5	1211.8	−0.19
140.671	1194.4	1190.8	0.30
143.435	1180.8	1177.7	0.26
144.309	1176.8	1173.6	0.28
148.167	1152.1	1155.2	−0.27
153.523	1126.9	1129.8	−0.26
158.903	1107.6	1104.3	0.30
165.910	1068.9	1071.0	−0.20
167.172	1062.8	1065.0	−0.20
172.343	1039.2	1040.4	−0.12
176.265	1021.0	1021.8	−0.08
180.501	1002.9	1001.7	0.12
185.304	980.3	978.9	0.15
190.685	952.0	953.3	−0.14
197.929	921.0	919.0	0.22

Correspondence concerning this Note should be addressed to R. A. Aziz.

ANALYSIS OF RESULTS

Hamann (1960) has shown that the reduction factor for velocity of sound V is

$$V_0 = \left(\frac{N_0\epsilon}{M}\right)^{1/2} \tag{3}$$

For classical liquids, whose effective intermolecular potential is a central and pair-wise additive one of the form

$$\phi = \epsilon f\left(\frac{\sigma}{r}\right) \tag{4}$$

the reduced velocity of sound V^* has the form

$$V^* = F_1(P^*, T^*) \tag{5}$$

where

$$V^* = V/V_0; \quad P^* = P/P_0; \quad T^* = T/T_0$$

Under saturated vapor pressure conditions, P^* is a function of T^* and V^* can be expressed as

$$V_\sigma{}^* = F_2(T^*) \quad [\sigma \text{ refers to saturated vapor conditions}] \tag{6}$$

That is, for a given reduced temperature T^*, liquids obeying the law of corresponding states should have the same $V_\sigma{}^*$.

Reduced velocity of sound data are plotted against reduced temperature in Figure 2 for CCl_2F_2 (this Note), CF_4 (Aziz et al., 1967) and CCl_4 (Rowlinson, 1959). The values of ϵ/k proposed by Nierode et al. (1970) for CCl_2F_2 (ϵ/k = 264.98 K) and for CF_4 (ϵ/k = 167.47 K) bring the reduced velocity curves $V_\sigma{}^*(T^*)$ for these two substances into coincidence; this lends support to their values. A value of ϵ/k = 377.1 K for CCl_4 is necessary to bring its reduced curve into close coincidence with those of CF_4 and CCl_2F_2. The deviation from coincidence is probably due to the fact that velocity data for CCl_4 were taken at constant pressure of one atmosphere. It was found that other sets of ϵ/k (Hirschfelder et al., 1963; Brunet and Doan (1970) did not give a satisfactory correlation. Recommended values of ϵ for velocity and temperature reduction are given in Table 2.

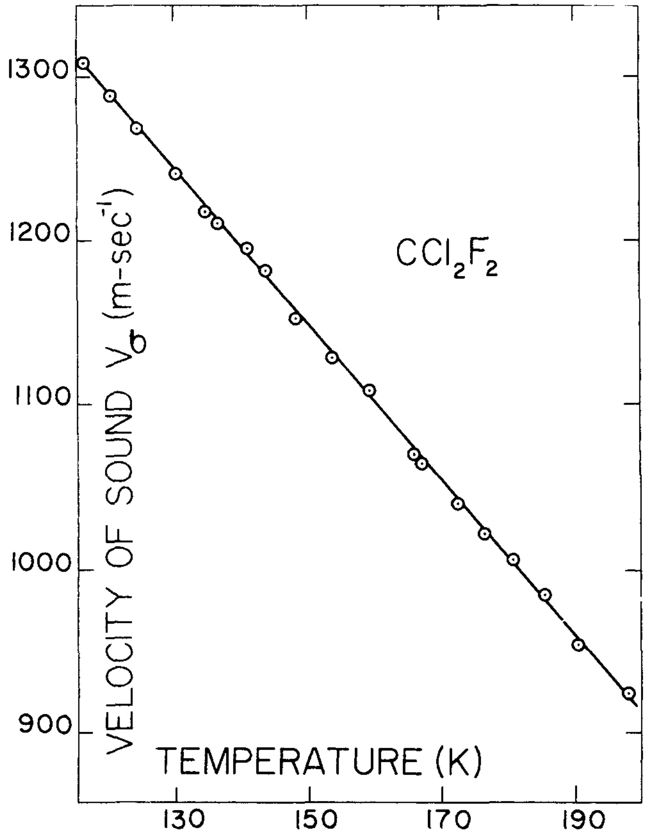

Fig. 1. Velocity of sound in liquid CCl_2F_2 under saturated vapor.

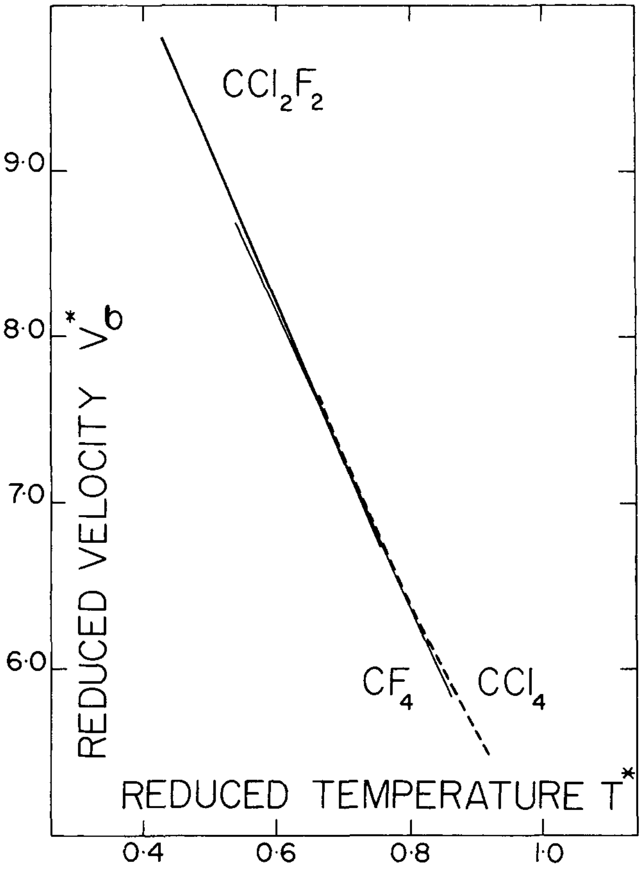

Fig. 2. Reduced velocity of sound versus reduced temperature CCl_2F_2 (ϵ/k = 264.98K); CF_4 (ϵ/k = 167.47K); CCl_4 (ϵ/k = 377.1K).

TABLE 2. RECOMMENDED ϵ VALUES AND REDUCTION FACTORS

Molecule	ϵ ($J \times 10^{-22}$)	$T_0 = \epsilon/k$ (K)	$V_0 = \left(\frac{N_0\epsilon}{M}\right)^{1/2}$ m/s
CCl_2F_2	36.582	264.98	134.99
CF_4	23.120	167.47	125.78
CCl_4	52.06	377.1	142.77

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NOTATION

C = third virial coefficient
k = Boltzmann constant
K = kelvins
M = molecular weight
N_0 = Avogadro's number
P = pressure
P^* = reduced pressure, $P^* = [P/(\epsilon/\sigma^3)]$

r = separation between molecules
T = thermodynamic temperature
T^* = reduced thermodynamic temperature, $T^* = [T/(\epsilon/k)]$
V = velocity of sound
V_0 = reduction constant for velocity of sound, $V_0 = (N_0\,\epsilon/M)^{1/2}$
V^* = reduced velocity of sound, $V^* = [V/V_0]$
V_σ = velocity of sound under saturated vapor conditions
V_σ^* = reduced velocity of sound under saturated vapor conditions

Greek Letters

ϵ, σ = intermolecular potential parameters
ϕ = intermolecular potential
ρ = density

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Stability of a Laminar Viscous Jet— The Influence of the Initial Disturbance Level

RALPH E. PHINNEY

Naval Ordnance Laboratory
Silver Spring, Maryland 20910

The instability and subsequent breakup of liquid jets projected into a gaseous atmosphere have been studied by many authors since the turn of the century. In particular, Fenn and Middleman (1969) have reported some significant recent experiments in which the ambient pressure for the jet was varied. Their results show some shortcomings of the stability analysis as normally applied. It has been traditional to assume that the initial disturbance level is constant with respect to exit velocity and with respect to disturbance wave number. The search has been for some new mode of instability or some extra parameter that will give an amplification rate that better fits the data. It is the purpose of this paper to examine critically the correlation of data and theory in this light. The outcome is the suggestion that the resolution of the difficulties is to correlate data by considering the initial disturbance level as variable.

THEORETICAL BACKGROUND

Jet stability theory assumes an axisymmetric, exponentially growing disturbance which ruptures the jet when its amplitude grows equal to the jet radius. As a result, the time-to-breakup T (which can also be interpreted as distance from the exit by knowing the jet velocity) is given by the relationship

$$T = \left(\frac{1}{\alpha}\right) \ln \left(\frac{D}{2\delta}\right) \qquad (1)$$

Grant and Middleman (1966) give an outline of the theory and a complete summary of progress in its application to this problem.

The problem reduces to that of finding a mathematical description for the forces causing breakup, and from this calculating the maximum amplification rate as a function of the physical parameters. In a few simple cases an analytic form can be found for α. In more complex cases a computer solution must be obtained for particular conditions. It is noteworthy that the analytic solution of Weber (1931), which does not include the effects of the ambient fluid, but which does include the jet viscosity, has been very successful in correlating data with low exit velocity (where the ambient effects are small). This success has spurred a search for a more complicated solution that would correlate a wider range of data. In particular, an explanation is sought for the observed fact that there always seems to be some critical point above which the breakup length stops increasing with exit velocity and starts to decrease.