

## Intermolecular Free Lengths in the Liquid State

### IV. Dependence on Temperature

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In the previous works in this series the applicability of the concept of free length has been elucidated<sup>1</sup>. Thus, it has been shown that properties such as compressibility, surface tension and viscosity can easily be related to the free length between the surfaces of the molecules in a pure liquid or liquid mixture. The fact that the concept of free length has not formerly been used in full probably depends on the difficulty of calculating it exactly. The definition hitherto used by us is not ideal as an error is included in it the magnitude of which varies with the temperature.

Owing to the importance of the free length for the understanding of intermolecular processes a systematic investigation has been made here of the temperature dependence of the free length. This problem is principally the same as to find a formula describing the thermal expansion of a liquid system. The thermal expansion is an intermolecular process and is mainly independent of the absolute magnitude of the molecules which is only slightly temperature dependent. Therefore we may anticipate a simpler relation between the free length and temperature than between the density (molar volume) and temperature. We have in this work set up an empirical formula which has been found to describe accurately the temperature dependence of the free length. Using this the corresponding expression for the density has been obtained. For practical purposes values have been calculated for plotting graphs from which the zero point density and the critical temperature of a liquid system can easily be obtained from its densities at two temperatures.

## RESULTS

When studying the temperature dependence of physical properties it is often convenient to compare the various substances in corresponding states. This is also the case when studying the intermolecular free length. The reduced free length is  $L_r = L_T/L_c$  where  $L_T$  is the free length at the temperature  $T$  and  $L_c$  is the free length at the critical temperature  $T_c$ . Systematic attempts have been made in order to correlate the reduced free length with the reduced temperature  $T_r$ . Various possible relations have been proposed which were tested using the following three equations.

1. The free length between the surfaces of spherical molecules in hexagonal packing is

$$L_T = (2^{1/2}/N)^{1/3} (V_T^{1/3} - V_0^{1/3}) \quad (1)$$

where  $N$  is Avogadro's number,  $V_T = M/\rho_T$  and  $V_0 = M/\rho_0$  are the molar volumes at  $T^\circ\text{K}$  and  $0^\circ\text{K}$ .

2. The radius of the spherical molecules in hexagonal close packing is

$$r_0 = 1/2(2^{1/2}/N)^{1/3} V_0^{1/3} \quad (2)$$

3. It is a known fact that for various substances there is generally a constant ratio between the densities at absolute zero and at the critical temperature  $\rho_0/\rho_c = 3.75$  (Partington<sup>2</sup>, p. 27). From this it follows that the free length at the critical temperature should be proportional to the molecular radius. Thus

$$L_c = cr_0 \quad (3)$$

where  $c$  is constant for different substances.

The various relationships between the reduced free length and the reduced temperature, tested by these equations, were obtained from known formulae applying to the reduced state and to the thermal expansion (Partington<sup>2</sup>). The following equation is the one best fitting experimental data

$$1 - L_r = (1 - T_r)^p \quad (4)$$

where  $p$  is constant,  $L_r$  the reduced free length and  $T_r$  the reduced temperature. To make possible an experimental test of equation (4) the following relation between density and temperature was derived from (1), (2), (3) and (4)

$$\rho_0 = \rho_T [1 + (c/2) - (c/2)(1 - T_r)^p]^{-3} \quad (5)$$

The values for the constants  $c$  and  $p$  can be determined in the following way. From equations (1), (2), (3) and (4) a relation between the constants can be obtained

$$c = 2(1-f)/[f-1 + (1-T_r)^p] \quad (6)$$

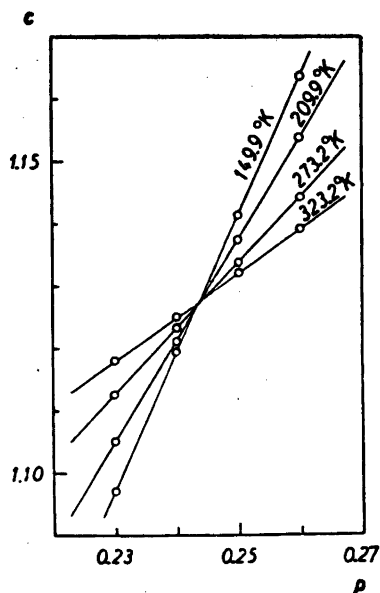


Fig. 1. Graphic determination of constants  $p$  and  $c$  for diethyl ether.

where  $f = (\rho_c/\rho_T)^{\frac{1}{p}}$  if  $\rho_c$  and  $\rho_T$  are the densities at  $T_c^\circ\text{K}$  and  $T^\circ\text{K}$ . By plotting  $c$  as a function of  $p$  for a substance at different temperatures a number of curves are obtained whose point of intersection gives the desired values for the constants. In Fig. 1 this is shown for diethyl ether, and in Table 1 a few examples are given of  $p$  and  $c$  values obtained for various unassociated compounds. The density values and critical temperatures were taken from Timmermans<sup>3</sup>. The average value for the exponent is  $p = 0.243$ . This value is not far from  $p = 1/4$  which value can be chosen without the accuracy of the

Table 1. Values obtained for the constants  $p$  and  $c$ .

Compound	$p$	$c$
Pentane	0.242	1.113
Hexane	0.240	1.117
Octane	0.236	1.150
Benzene	0.246	1.110
Difluorodichloromethane	0.250	1.128
Bromobenzene	0.244	1.124
Carbon tetrachloride	0.249	1.106
Ethyl acetate	0.240	1.155
Diethyl ether	0.244	1.128

proposed equations being reduced. The two corresponding values for the constants thus used in this work are

$$\begin{aligned} p &= 1/4 \\ c &= 1.092 \end{aligned} \quad (7)$$

An experimental test of the proposed formulae was thus possible. If equation (4) is valid constant values for the zero point densities  $\rho_0$  according to equation (5) should be obtained if the calculations are made at different temperatures. Such calculations were made for compounds other than those given in Table 1 and for which accurate density values were available between the melting point and critical temperature. The compounds 2-methylbutane, heptane, toluene, methylcyclohexane, carbon tetrachloride, chlorobenzene, methyl formate and ethyl mercaptan were investigated as well as octane which has  $c$  and  $p$  values differing most from those given in (7). The average deviation of the  $\rho_0$  values for all compounds, each studied at five different temperatures, was 0.28 per cent. The corresponding value for octane was 0.15 per cent, the smallness of which justifies the choice of the constants according to (7). Equation (5) describes the change of density with temperature more accurately than any of the corresponding formulae previously suggested (Partington<sup>2</sup>, Sec. VIII B, C). The values obtained for the zero point densities are generally 4.3 per cent higher than those calculated from Sugden's formula<sup>4</sup>. But, as more constant values are obtained for each compound when calculated at widely different temperatures, our method of calculating the zero point densities is regarded as preferable.

The equations were also tested on liquid mixtures in the following way. The critical temperature and zero point density were calculated for each mixture by equation (5) from experimentally determined densities (Smyth *et al.*<sup>5</sup>) at two temperatures as described below. Densities then were calculated from (5) for other temperatures and were compared with those experimentally determined. Mixtures of the type heptane — ethylene chloride, heptane — ethyl acetate and heptane — butylbromide were investigated in the temperature range  $-90^\circ$  to  $+70^\circ$  C or  $-90^\circ$  to  $+90^\circ$  C at intervals of  $20^\circ$  C. The average deviation in the calculated density values for different temperatures and mixtures was 0.12 per cent. From that it can be concluded that non-associated liquid mixtures follow equation (4) and (5) with good accuracy.

#### DISCUSSION

It should be observed that the proposed equation (4) between the free length and the temperature is completely empirical. No satisfactory theoretical deduction could be obtained. However, in view of the accuracy with which the

Table 2. Values for plotting  $\rho_0/\rho_T$  as a function of  $T/T_c$  according to equation (5) and  $L_T/V_T^{1/3}$  as a function of  $T/T_c$  according to equation (8).  $L$  is measured in Å,  $V_T$  in ml and the temperatures in degrees Kelvin.

$T/T_c$	$\rho_0/\rho_T$	$L_T/V_T^{1/3}$	$T/T_c$	$\rho_0/\rho_T$	$L_T/V_T^{1/3}$
0.300	1.1463	0.0591	0.575	1.3498	0.1267
0.325	1.1612	0.0646	0.600	1.3742	0.1336
0.350	1.1768	0.0702	0.625	1.4002	0.1411
0.375	1.1928	0.0759	0.650	1.4278	0.1488
0.400	1.2095	0.0816	0.675	1.4573	0.1568
0.425	1.2269	0.0876	0.700	1.4894	0.1652
0.450	1.2451	0.0938	0.725	1.5233	0.1740
0.475	1.2640	0.0999	0.750	1.5606	0.1832
0.500	1.2839	0.1062	0.775	1.6015	0.1931
0.525	1.3048	0.1128	0.800	1.6467	0.2036
0.550	1.3267	0.1195			

equation holds, it seems likely that it should be possible to give a theoretical deduction of this or a similar equation.

As the free length cannot be measured directly it was indirectly inferred, from the good agreement between experimental data and equation (5), that equation (4) is also valid with the same accuracy. The presumption for this is the validity of equations (1), (2) and (3). Of these (1) and (2) are simple stereometric formulae derived assuming spherical molecular shape and hexagonal packing. This is an oversimplification of the actual conditions. However, the influence of molecular shape on the free length has been studied previously and it was found that for low molecular weight substances the molecules can be regarded as spheres<sup>1</sup>. On the other hand form factors must be introduced when studying macromolecular compounds. The form of packing has even less influence on the equations (1) and (2). For cubical packing identical equations are obtained. Equation (3) is based on experimental data and the applicability of it is further illustrated by the good agreement in  $c$  values obtained for various compounds as shown in Table 4. For these reasons equation (4) can be regarded as valid.

For the practical use of the given equations it is convenient to make the calculations graphically. Values for drawing commonly used curves are given in Tables 2 and 3. If the zero point density  $\rho_0$  is required the ratio  $\rho_0/\rho_T$  is first graphically calculated from the reduced temperature. If the

Table 3. Values, calculated from equation (5), for plotting the critical temperature  $T_c$ , °K as a function of the ratio  $\rho_1/\rho_2$  of the densities at two temperatures  $t_1$  and  $t_2$ , °C.

$T_c$ (°K)	$\rho_1/\rho_2$						
	$t_1 = 0$ $t_2 = 15$ (°C)	$t_1 = 0$ $t_2 = 20$ (°C)	$t_1 = 0$ $t_2 = 30$ (°C)	$t_1 = 15$ $t_2 = 25$ (°C)	$t_1 = 15$ $t_2 = 30$ (°C)	$t_1 = 20$ $t_2 = 30$ (°C)	$t_1 = 20$ $t_2 = 60$ (°C)
400	1.03392	1.04614	1.07229	1.02422	1.03714	1.02498	1.11727
425	1.02920	1.03960	1.06152	1.02054	1.03137	1.02109	1.09571
450	1.02572	1.03481	1.05382	1.01811	1.02739	1.01835	1.08143
475	1.02301	1.03109	1.04793	1.01601	1.02434	1.01632	1.07114
500	1.02088	1.02819	1.04320	1.01444	1.02191	1.01465	1.06330
525	1.01907	1.02572	1.03944	1.01320	1.01999	1.01338	1.05704
550	1.01765	1.02376	1.03631	1.01211	1.01835	1.01226	1.05209
575	1.01640	1.02206	1.03367	1.01120	1.01698	1.01135	1.04803
600	1.01538	1.02043	1.03143	1.01048	1.01583	1.01057	1.04450
625	1.01438	1.01926	1.02935	1.00978	1.01477	1.00990	1.04155
650	1.01353	1.01811	1.02764	1.00921	1.01395	1.00936	1.03895
675	1.01285	1.01723	1.02617	1.00888	1.01320	1.00879	1.03658
700	1.01211	1.01632	1.02477	1.00827	1.01250	1.00833	1.03456
725	1.01156	1.01550	1.02355	1.00785	1.01184	1.00794	1.03275
750	1.01109	1.01480	1.02248	1.00746	1.01129	1.00755	1.03113
775	1.01057	1.01413	1.02145	1.00716	1.01078	1.00722	1.02969
800	1.01011	1.01353	1.02054	1.00683	1.01032	1.00692	1.02838
900	1.00863	1.01156	1.01750	1.00580	1.00876	1.00586	1.02404
1 000	1.00755	1.01008	1.01532	1.00508	1.00770	1.00514	1.02096

free length  $L_T$  is required at a certain temperature the ratio  $L_T/V_T^{\frac{1}{3}}$  is first graphically obtained from the reduced temperature according to

$$L_T = V_T^{\frac{1}{3}}(2\frac{1}{N})^{\frac{1}{3}}[1 - (1 - T_r)^2]/[1 + (2/c) - (1 - T_r)^2] \quad (8)$$

which equation has been obtained from (2), (4) and (5).

If the critical temperature is unknown for a liquid system, it can easily be obtained graphically from (5) if two densities  $\rho_1$  and  $\rho_2$  are known at two temperatures  $T_1$  and  $T_2$ , °K ( $t_1$  and  $t_2$ , °C). The ratio  $\rho_1/\rho_2$  is plotted as a function of  $T_c$  for the two temperatures. Some values are given in Table 3 which have been calculated using  $-273.2^\circ\text{C}$  as the value of the absolute zero. Some examples of calculated critical temperatures are given in Table 4. The average error for 18 non-associated compounds is 1.4 per cent. This method of calculating the critical temperature is of special interest for the study of associated liquids which will be treated in a subsequent work.

Table 4. Critical temperatures calculated from the ratio of densities at two temperatures  $\rho_{t_1}/\rho_{t_2}$ .

Compound	$\rho_{t_1}$ at ( $t_1$ °C)	$\rho_{t_2}$ at ( $t_2$ °C)	$T_c$ (°K) Calc. from $\rho_{t_1}/\rho_{t_2}$	$T_c$ (°K) Calc. mean value	$T_c$ (°K) Expt. observed	Per cent deviation
Hexane	0.67704 (0°)	0.66380 (15°)	512			
	0.67704 (0°)	0.65055 (30°)	516			
	0.6593 (20°)	0.6502 (30°)	508	512	508.0	+ 0.7
Cyclohexane	0.78310 (15°)	0.76928 (30°)	558			
	0.78310 (15°)	0.74060 (60°)	555			
	0.77853 (20°)	0.76914 (30°)	552	555	553.9	+ 0.2
Benzene	0.89996 (0°)	0.88420 (15°)	548			
	0.88420 (15°)	0.86844 (30°)	554			
	0.8790 (20°)	0.8357 (60°)	552	551	561.7	- 1.9
Chlorobenzene	1.12792 (0°)	1.09550 (30°)	623			
	1.1062 (20°)	1.0955 (30°)	638			
	1.1062 (20°)	1.0636 (60°)	640	633	632.4	0.0
Ethyl acetate	0.92453 (0°)	0.90657 (15°)	515			
	0.90657 (15°)	0.88851 (30°)	521			
	0.90665 (15°)	0.89446 (25°)	517	518	523.3	- 1.0
Diethyl ether	0.73622 (0°)	0.71925 (15°)	468			
	0.71925 (15°)	0.70205 (30°)	472			
	0.71930 (15°)	0.70768 (25°)	470	470	466.8	+ 0.7

Sometimes it is of interest to know the temperature derivative of the free length

$$dL_T/dT = p(L_c/T_c)(1-T_c)^{p-1} = p(L_c-L_T)/(T_c-T) \quad (9)$$

The equations given in this work for calculating the free length and the zero point densities should replace those previously used if good accuracy is required. The formulae obtained make possible an exact study of the temperature dependence of intermolecular properties by relating them to the free length. For instance, it has appeared that the fluidity for non-associated liquids is a strictly linear function of the free length within large temperature ranges.

#### SUMMARY

The reduced free length in a liquid system  $L_r = L_T/L_c$  is related to the reduced temperature  $T_r = T/T_c$  by the equation  $1-L_r = (1-T_r)^p$  where  $L_T$  and  $L_c$  are the intermolecular free lengths at the temperature  $T$  and at the

critical temperature  $T_c$  respectively. The molecular radius is  $r_o = L_c/c$ . As  $p$  and  $c$  vary only slightly with different compounds they can be put equal to 1/4 and 1.092, respectively. From this equation formulae were derived which make possible calculations of zero point densities and critical temperatures for a liquid system if the densities at two different temperatures are known. Values are given for plotting curves for graphical computations of such data. Knowledge of the temperature dependence of the free length is of value for the study of intermolecular properties and processes.

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