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DERIVING THE EQUATION OF STATE FOR LIQUIDS AND EXTENSION OF THE PRINCIPLE OF CORRESPONDING STATES

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Abstract

A new simple model is introduced for a liquid and an equation of state is derived based on this model and the statistical mechanical calculations. This equation of state works well for the non-polar and slightly polar liquids. The important conclusion that may be deduced from this equation of state is that if the reduced variables of state are chosen and defined appropriately, then, the principle of corresponding states works well for liquids, and it may even be unnecessary to use an additional parameter like the acentric factor.

Introduction

A liquid has a short-range order that shows up in diffraction effects when X-ray is scattered by the liquid. In other words, a liquid has neither the long-range structural order of a solid nor the small intermolecular interaction energy of a gas. While the gas molecules are distributed almost randomly because of such small intermolecular interactions, there is some local ordering in a liquid. The size of the local ordering in a liquid depends on the temperature and the magnitude of the intermolecular interactions among the molecules. Hence, the theoretical studies of liquids are much more complicated than those of solids and gases.

A model which has been used frequently in the theoretical studies of liquid is the hard-spheres model. Using Monte Carlo [1] and molecular dynamics [2] calculations upon finite systems, this model has been effectively employed to derive a simple analytical equation of state. The result of these calculations is an equation for PV/RT as a function of V/V_0, where V_0 is the volume of spheres in a close-packed lattice. In other calculations [3-6], the attractive energies in a fluid are treated as a perturabation upon the hard-sphere infinite repulsion. Using this approximation, it has been found that the leading term of the correction to the hard-sph pressure, P_{hs}, is proportional to the second power of t density of the fluid.

There is no general simple analytical equation state to be valid for liquids. As for the imperfect gas several empirical equations of state have been propos for liquids, and those which are more important will recalled here. Longuet-Higgins and Widom [7] propos the following equation of state from expli combination of the hard-sphere results and the Van d Waals energy (-a/V),

$$P=P_{hs}-\frac{a}{V^2}$$

Another equation of state for liquid proposed Huddleston [8],

$$\ln\left(\frac{PV^{2/3}}{V_0^{1/3}-V^{1/3}}\right)=A+B(V_0^{1/3}-V^{1/3})$$

where V_0 is the molar volume at "zero" pressure a A and B are some positive constants. Cho [9] propos the following equation of state for liquids,

$$\frac{V}{V_0}=\frac{K+P_0}{(K+P)^C}$$

where V_0 is the value of V at T and P_0, a referen

Keywords: Equation of state, Corresponding states, Acentric factor

pressure, and

$$B_T = -V\left(\frac{\partial P}{\partial V}\right)_T \ , \ G = \left(\frac{\partial B_T}{\partial P}\right)_T \ , \ C = \frac{1}{G}$$

$$B_T = B(T) + GP \ , \ K = \frac{B(T)}{G}$$

And finally the Tait equation [10-11] and its modification by Kirkwood may so far be the best empirical representation of the equation of state for liquids. Tait's equation is given by,

$$\ln\left(\frac{P+L(T)}{P_0+L(T)}\right) = n\left(\frac{V_0 - V}{V_0}\right)$$

where P_0 is some standard pressure, V_0 is the corresponding liquid volume, L(T) is a function of temperature, and n is a constant whose value depends on the specific liquid.

Liquid may be studied theoretically by using statistical mechanics as well. Statistical mechanical theories of liquid fall into two catagories: One is the hole theory which was formulated by Eyring in the 1930s. This theory has undergone many modifications and extensions, with the latest extensions being undertaken in the 1960s, and is called the theory of significant structures. In this theory, a liquid is considered to be made of a solid-like part and a gas-like part (where the partition functions are known for both parts). Other theories (in statistical mechanics) for the liquid state are called the cell theories. According to these theories, a liquid can be represented by a solid where, instead of just vibrating about its lattice site, each atom (or molecule) is allowed to move within a cage or a cell whose boundaries are defined by the position of its nearest neighboring atoms. For more information in this regard the reader is referred to McQuarrie [12].

Model And Calculation of Energy and Entropy

Consider a liquid at temperature T with N atoms (molecules) and Volume V. Our model is based on the following assumptions:

(i) Consider a close-packed lattice with M sites and the volume v at temperature T. We assume (for the time being) that the atoms in the liquid do not move around and must be distributed among these sites. Such a distribution may be done in g ways, where,

$$g = \frac{M!}{N!\,(M-N)!}$$

The configurational entropy of such a system may be calculated by using the Boltzmann equation, S=kln g, the entropy in terms of θ_S , $\theta_S = N/M$, is given by,

$$S = -\frac{NK}{\theta_S}\left\{\theta_S \ln \theta_S + (1-\theta_S) \ln (1-\theta_S)\right\} \quad (1)$$

(ii) The subscript "s" on θ is used because molecules are assumed to be solid-like (do not move around). Replacing θ_S by θ_l, expression (1) then can be used for the liquid, and hence,

$$S = -\frac{Nk}{\theta_l}\left\{\theta_l \ln \theta_l + (1-\theta_l) \ln (1-\theta_l)\right\} \quad (2)$$

In both cases, θ will be proportional to 1/V, because M is proportional to V. Therefore,

$$\theta_l = \frac{\alpha_l}{V} \quad (3)$$

where α_l is the proportionality constant. α_l depends on the state of the system. Now we have to find the parameters that α_l may depend on. As we know, the molar entropy of liquids (S/Nk) is usually large (more than 12 entropy units [13], then $\theta_l \ll 1$, and equation (2) may be reduced to

$$S = Nk(1 - \ln \theta_l) \quad (4)$$

(iii) In order to find the parameter(s) that the proportionality constant α_l depends on, and to see how it is related to these parameters, we may write S in terms of T and V. From classical thermodynamics,

$$dS = C_V d \ln T + \frac{1}{T}\left\{P + \left(\frac{\partial U}{\partial V}\right)_T\right\} dV$$

where U is the internal energy, and C_V is the hea capacity at constant volume. The above equation may b written as,

$$dS = C_V d(\ln T) + \frac{\Delta C}{\alpha T} d(\ln V) \quad (5)$$

where $\Delta C = C_P - C_V$, and α is the isobaric therm expansivity. The change in the volume of a liquid i small, the second term then may be negleted. C_V of liquid depends slightly on T [8]. Equation (5) may the be integrated to,

$$S = C_V \ln T + \text{constant} \quad (6)$$

where the volume dependence of entropy, which assumed to be constant, is included in the constant term

By comparing equation (4) with (6), we get,

$$\theta_l = \frac{\beta_l}{VT^m} \quad (7)$$

where β_l and m are some positive constants and th values are unimportant here.

Actually the expression given in equation (2) for the entropy of a liquid gives translational entropy alone. The contribution due to the other degrees of freedom, S_{oth} (T), depends only on T. Therefore, the total entropy of a liquid may be given by,

$$S = \frac{Nk}{\theta_1}\left\{\theta_1 \ln \theta_1 + (1-\theta_1)\ln(1-\theta_1)\right\} + S_{oth}(T) \tag{8}$$

(iv) We assume that the same intermolecular interactions apply to each molecule and each one interacts only with its nearest neighbors, the number of which is equal to C. The internal energy of the liquid is then given by,

$$U = \frac{1}{2}CN\varepsilon + E_K(T) \tag{9}$$

where ε is the potential energy of a pair of the nearest neighbor, $E_K(T)$ is the kinetic energy of all molecules which depends only on T, and $\frac{CN}{2}$ is the number of pairs. Here, we have actually assumed that the force between any two molecules is independent of the configuration of all other molecules present. This assumption is generally valid, except for molecules which tend to associate (like molecules with hydroxyl or amino group, [11]).

The equations which have been derived here for the nternal energy and the entropy will be used later on.

The Equation of State

By using the above model, the Helmholtz free nergy, A, can be calculated. The entropy and the nternal energy are given in equation (8) and (9) espectively. The free energy is given by,

$$A = \frac{1}{2}CN\varepsilon + E_k(T) + \frac{NkT}{\theta_1}\left\{\theta_1\ln\theta_1 + (1-\theta_1)\ln(1-\theta_1)\right\} - TS_{oth}(T) \tag{10}$$

The equation of state can be derived by using,

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} \tag{11}$$

Before carrying out the above derivative, however, e pair potential (ε) should be expressed in terms of V. We may use any realistic function for ε in terms of the termolecular distance, r. One of these functions is the nnard-Jones (6-12) Potential, which is good enough r the representation of the potential energy of a pair of npolar and slightly polar molecules, and is given by,

$\varepsilon = A_1/r^{12} - B_1/r^6$

or in terms of V; $\varepsilon = A_2/V^4 - B_2/V^2$ (12)

(That is because of the fact that the average distance between the nearest neighbors, r, is proportional to $V^{1/3}$, for constant N).

By substituting ε from equation (12) into equation (10), and taking the partial derivative of A with respect to V, by using equation (11), the following equation will be obtained.

$$P = \frac{A_3}{V^5} - \frac{B_3}{V^3} - \frac{NkT}{\theta_1 V}\ln(1-\theta_1) \tag{13}$$

But since $\theta_1 << 1$, equation (13) is reduced to,

$$P = \frac{A_3}{V^5} - \frac{B_3}{V^3} + \frac{NkT}{V} \tag{14}$$

where A_3 and B_3 parameters depend on T.

In order to evaluate the model, we must see how well the experimental P,V,T data fit into equation (14). It should be noticed that when the volume of the fluid approaches infinity, the equation of state approximates to PV=NkT, which is expected, since the fluid approaches the ideal gas. In order to see how well the experimental P,V data fit into the isotherms of equation (14), we may rearrange equation (14) to,

$$(Z-1)V^2 = \frac{(A_3/NkT)}{V^2} - \frac{B_3}{NkT}$$

or,

$$(Z-1)V^2 = \frac{A_4}{V^2} - B_4 \tag{15}$$

where $A_4 = A_3/NkT$, $B_4 = B_3/NkT$, and Z is the compressiblility factor of the fluid.

If the model is appropriate for a fluid, then the plots of $(Z-1)V^2$ against $1/V^2$ must be linear for the isotherms of that fluid. The actual values of Z for different reduced temperatures and pressures are tabulated by Pitzer et al. [14]. Actually the quantities which are denoted by Z_o and Z_1 are tabulated in reference [14]. Z is related to Z_o and Z_1 as,

$$Z = Z_o + \omega Z_1 \tag{16}$$

where ω is the acentric factor.

We first carried out the calculation for Ar. One sample of such calculations is given in Table 1, for $T_r = 0.8$. The values for pressure in the second column of this table are calculated by

P_r	P/atm	Z_0^*	$-Z_1^*$	Z	V/lit $mole^{-1}$	V_r	$(Z-1)V_r^2$	$\frac{1}{V_r^2}$
.6	28.8	.100	.044	.100	.0344	.4582	-.1889	4.7633
.8	38.4	.133	.058	.133	.0343	.4570	-.1811	4.7872
1.0	48.0	.164	.07	.164	.0338	.4509	-.1699	4.9195
2.0	96.0	.318	.13	.318	.0328	.4371	-.1303	5.2337
4.0	192.0	.605	.23	.605	.0312	.4158	-.0683	5.7838
6.0	288.0	.883	.29	.884	.0304	.4050	-.0190	6.0954
8.0	384.0	1.150	.35	1.151	.0297	.3955	+.0236	6.3920

* data are taken from ref. [14]

Table 1. The compressibility factor, Z, V_r, and $(Z-1)\ V_r^2$ for liquid Ar for $T_r = 0.8$.

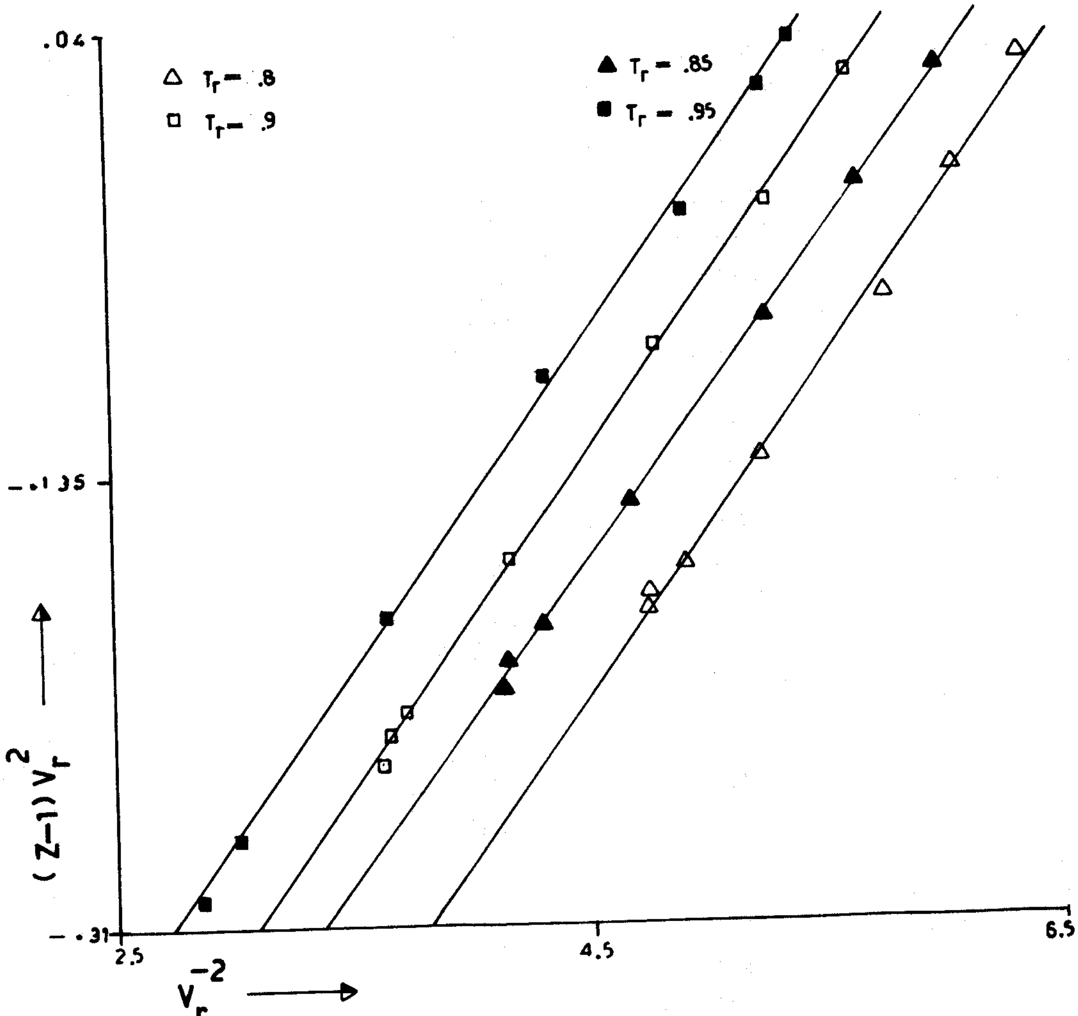

Figure 1. The quantity $V_r^2\ (Z-1)$ versus $1/V_r^2$ for liquid Ar for T_r = .8,.85,.9, and .95.

$$P = P_r\ P_c$$

where, for Ar, $P_C = 48.00$ atmosphere. The values for the next two columns (Z_0 and Z_1) are taken directly from reference [14]. Z is calculated from

$$Z = Z_0 + \omega\ Z_1$$

where, for Ar,$\omega = -0.002$. The values for volume is calculated from

$$V = \frac{ZRT}{P}$$

Where $T = T_r T_c =$ (0.8) (150.72K) = 120.576K. The reduced volume (V_r) is calculated from,

$$V_r = \frac{V}{V_c}$$

Where $V V_c = Z_c RT_c / P_c$, and for Ar at $T = T_c$,

$$V_c = \frac{(0.291)\,(0.0821)\,(150.72)}{48} = 0.075018 \text{ lit mol}^{-1}$$

We carried out similar calculations for liquid Ar with T_r = 0.85,0.90,0.95, and 1.00, and also for gaseous Ar with T_r = 1, and 2, and plotted the quantity V_r^2 (Z-1) against $1/V_r^2$ in Figures 1, 2, and 3 by computer. These plots show that the liquid phase data fit well into the equation of state up to temperature close toT_r = 1.0. However, the data of the gas phase do not fit into the equation (15) at all, and the points do not lie on a straight line. So at this stage, one may conclude that the model is appropriate for liquids but not for gases, and may be tested for other liquids as well.

We then carried out similar calculations for more than ten other liquids with T_r = .8 (the necessary data

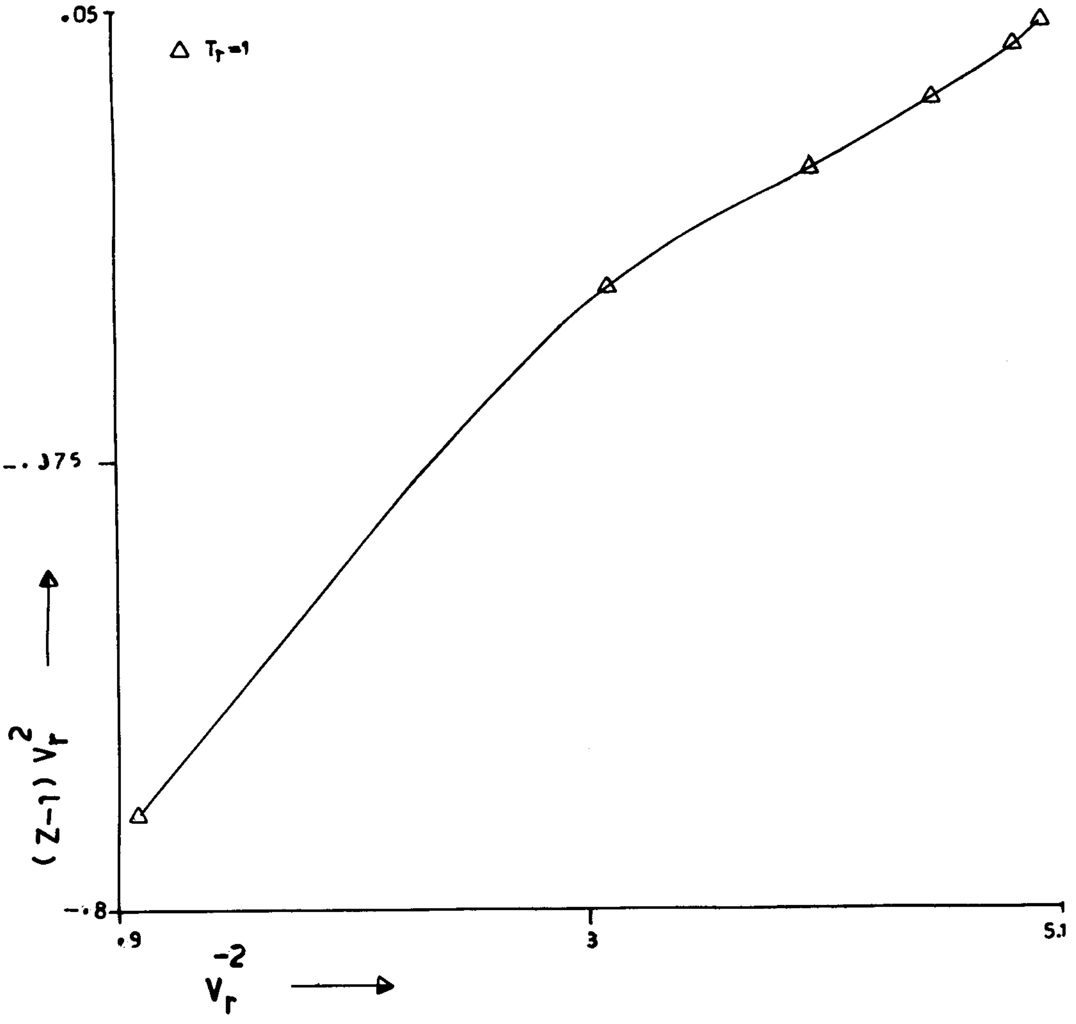

Figure 2. The quantity V_r^2 (Z-1) versus $1/V_r^2$ for liquid Ar for T_r=1.

Substance	B_4	A_4	V_0/lit mol^{-1}	$10^5\ \sigma^2$
Ar	.7995	.1281	.0300	2.10
Kr	.7995	.1281	.0369	2.10
Xe	.7826	.1249	.0479	2.10
CH_4	.7999	.1277	.0396	1.34
N_2	.7938	.1256	.0354	1.54
H_2S	.8100	.1270	.0387	4.24
C_2H_6	.8219	.1293	.0575	3.21
C_3H_8	.8441	.1310	.0796	5.54
neopentane	.8467	.1302	.1220	7.93
n-Butane	.8636	.1336	.1007	5.73
C_6H_6	.8521	.1314	.1021	9.14
CO_2	.8668	.1324	.0367	7.45
n-C_5H_{12}	.8953	.1372	.1218	9.08
n-C_7H_{16}	.8341	.1226	.1664	11.6

Table 2. The values of A_4, B_4, V_0, and the variance, σ^2, for different liquids for T_r=0.8.

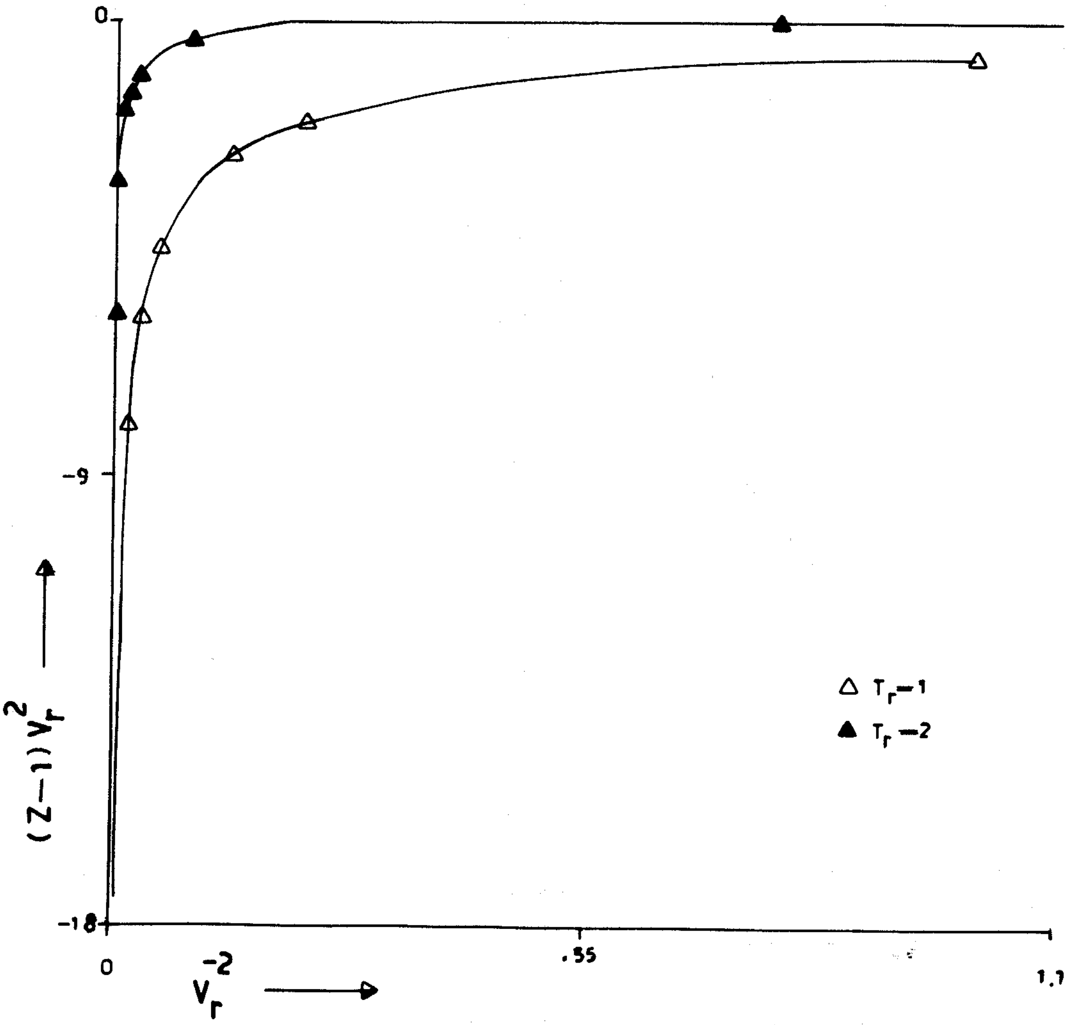

Figure 3. The quantity V_r^2 (Z-1) versus $1/V_r^2$ for gaseous Ar for T_r=1 and 2. .

are taken from reference 14). The results are plotted in figures 4, 5, and 6. The values for the intercept, B_4 , and the slope, A_4, are listed in Table 2 for all lines, along with the variance, σ^2, for $T_r = .8$. The fact that the curves in these figures are all relatively good straight lines proves that our model works well for these liquids. Even though the reduced variables have been used to plot these figures, the lines are not superimposed. The reason for such behavior will be considered in the following section.

Principle of the Corresponding States

The classical principle of the corresponding states was introduced first by J.D. Van der Waals in 1880, in connection with the equation of state and the critical constants of gases. The statistical mechanical version of this principle was firmly established in the period 1939-1950. However, the remarkable scope and accuracy of this principle have begun to be fully appreciated in the past twenty years [15-17]. According to this principle, if the compressibility factor Z is expressed in terms of the reduced variables (P_r and T_r) then all substances show the same behavior, and we will have a universal function for $Z = Z(T_r, P_r)$. However, more accurate data show that these functions do not superimpose on each other. In other words Z depends on the specific substance, as well as on T_r and P_r . It is for this reason that a third parameter, which is called the acentric factor, is introduced as the third variable for the function Z. It is believed that the three parameter function may well yield at least a factor of ten greater accuracy than those obtained from the simple two parameter function [14]). It is said (by Pitzer, et al., [14] that the reason for suggesting the acentric factor is the important deviation that arises from the fact that the sum of the inverse sixth power term applying to the various portions of a pair of complex molecules can not be replaced by a single inverse sixth power term in the distance between molecular centers. We focus our attention here on this point.

Let us start with the equation of state for liquids, equation (14), and derive its reduced form. We set the first and the second partial derivatives of P with respect to V equal to zero, where these constraints must be satisfied at the critical point. Hence, for the critical point, where $V = V_C$, $P = P_C$ and $T = T_C$, we have,

$$\frac{\partial P}{\partial V} = -\frac{5A_3}{V^6} + \frac{3B_3}{V^4} - \frac{RT}{V^2} = 0$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{30A_3}{V^7} - \frac{12B_3}{V^5} + \frac{2RT}{V^3} = 0$$

$$P = \frac{A_3}{V^5} - \frac{B_3}{V^3} + \frac{RT}{V}$$

The general solutions to the above equations are,

$$A_3 = \frac{RT_C}{5} V_C^4 \, , \; B_3 = \frac{2}{3} RT_C V_C^2 \, , \; R = \frac{15P_C V_C}{8T_C} \qquad (17)$$

Now, if A_3, B_3 and R are substituted into the equation of state and P,V, and T are replaced by $P_r\, P_C$, $V_r\, V_C$, and $T_r\, T_C$ respectively, then, the reduced form of the equation of state will be obtained as,

$$P_r = \frac{1}{5Z_C}\left(\frac{1}{V_r^5}\right) - \frac{2}{3Z_C}\left(\frac{1}{V_r^3}\right) + \frac{T_r}{Z_C}\left(\frac{1}{V_r}\right) \qquad (18)$$

On the one hand if the above equation is solved for V_r, we get the following result:

$$V_r = V_r\,(P_r, T_r, Z_C) \qquad (19)$$

On the other hand if similar substitutions are made (for A_4, B_4, and V) in equation (15) the following result will be obtained,

$$(Z - 1)\, V_r^2 = \left(\frac{1}{5T_r}\right) \frac{1}{V_r^2} - \frac{2}{3T_r} \qquad (20)$$

If V_r is substituted from equation (19) into equation (20), and then the resultant equation is solved for Z, the final result would be as,

$$Z = Z\,(P_r, T_r, Z_C) \qquad (21)$$

Even though the attraction term between pairs of molecules has been treated here as the inverse of sixth power term, the function $Z=Z\,(T_r, P_r)$ is not obtained as a universal function. This is due to the fact that Z_C has different values for different fluids, an important conclusion which ought to be kept in mind. Equation (20) shows, however, that the function $Z=Z\,(T_r, V_r)$ is a universal function. We should then present Z in terms of V_r and T_r rather than P_r and T_r . We have plotted the quantity $(Z - 1)\, V_r^2$ versus $1/V_r^2$ in Figures 4, 5, and 6 for different liquids. The lines do not superimpose, however. Two different conclusions may come out of these figures. One is that the model (and hence the equation of state) is not accurate, and the second is that

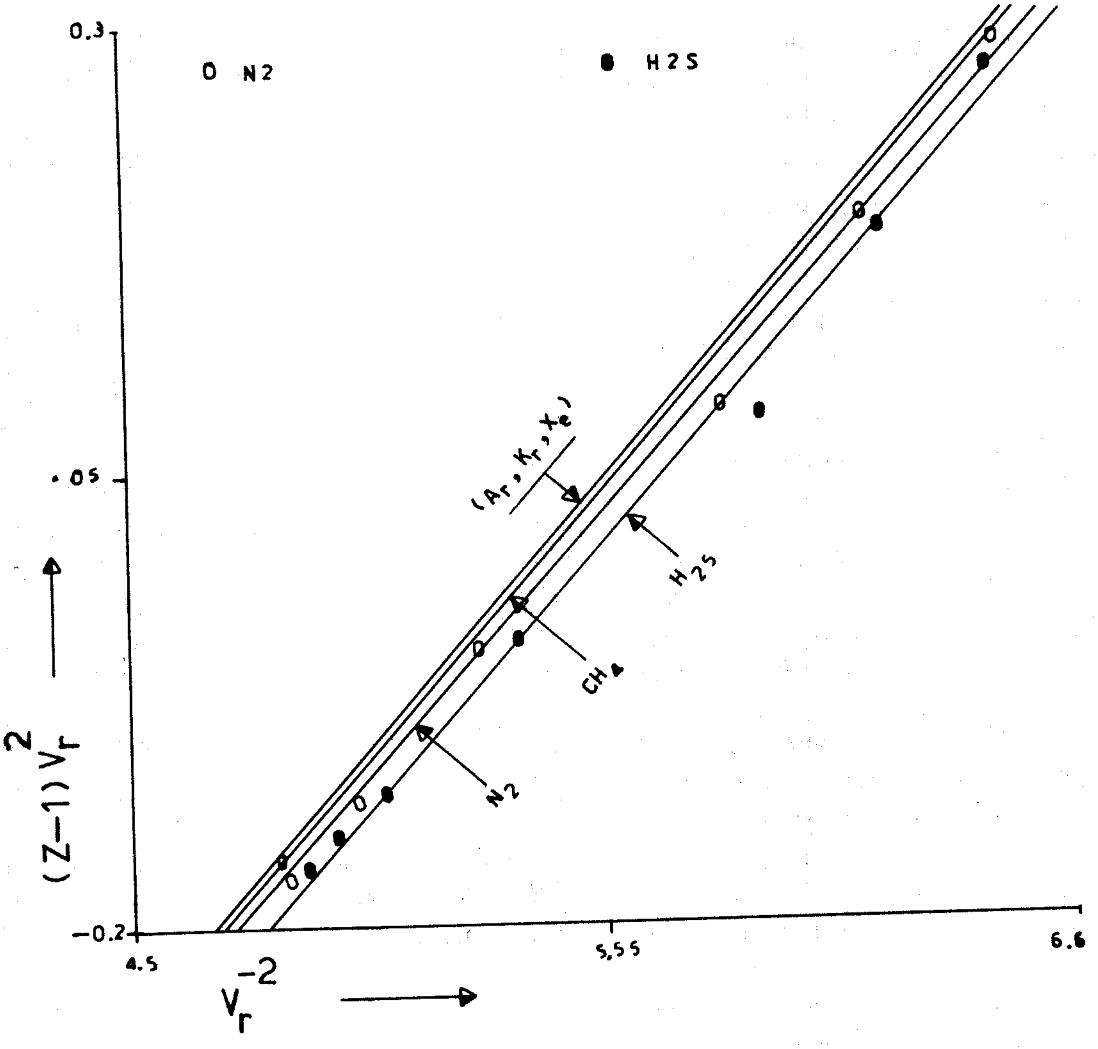

Figure 4. The quantity V_r^2 (Z-1) versus $1/V_r^2$ for six different liquids (T_r=0.8).

the dimensionless quantities (specifically V_r) are not appropriately defined. Since it has already been shown that our model works well for these liquids, the former conclusion may then be discarded, and the latter conclusion should be seriously considered.

It seems logical to choose the reference state as one that two nearest neighbor molecules have similar interaction in all liquids, instead of the critical state. An appropriate and practical choice is the state in which the attraction cancels out the repulsion. This state corresponds to Z=1. We denote the molar volume of liquid in this state by V_0 (the subscript zero means no net interaction). We then define the new dimensionless volume as $V_r = \frac{V}{V_0}$. Now we replace V by V_r in equation (15), which gives,

$$(Z - 1)\, V_r^2 = \frac{A_r}{V_r^2} - B_r \qquad (22)$$

where A_4 and B_4 are replaced by A_r and B_r respectively.

For a given isotherm, V_0 can be calculated by using equation (15) in its reduced form, and solve that equation for V_r at Z=1. The result is,

$$\frac{1}{V_r^2} = \frac{B_4}{A_4} \qquad (23)$$

By knowing the values for B_4 and A_4, which are given in Table 2 for T_r = 0.8, then V_r can be calculated at Z=1. If this value of V_r is multiplied by V_C the value of V_0 will be obtained for that isotherm. For example, for liquid Ar with T_r =0.8, B_4=0.7995 and

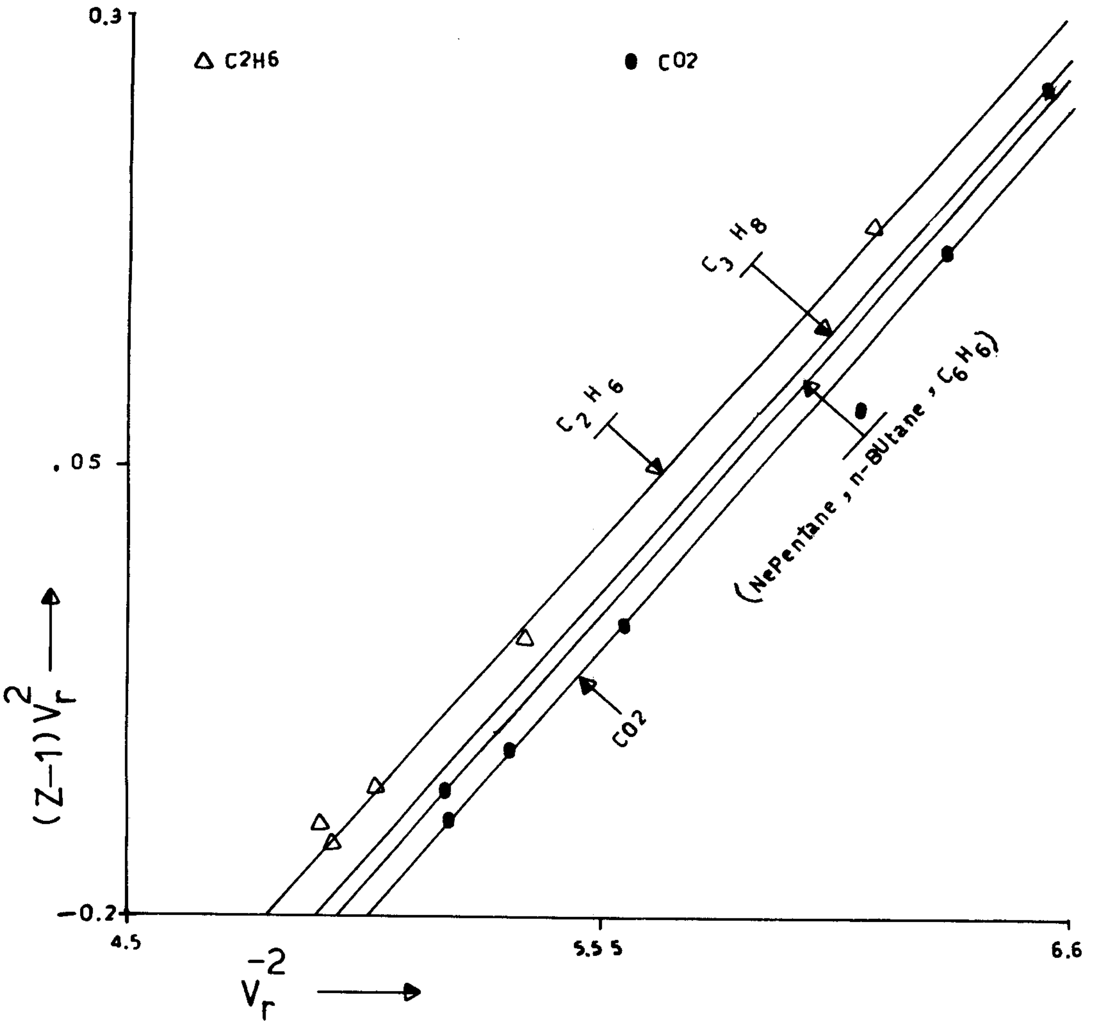

Figure 5. The quantity V_r^2 (Z-1) versus $1/V_r^2$ for six different liquids (T_r =0.8).

A_4=0.1281 (see table 2), then at Z=1,

$$\frac{1}{V_r^2} = \frac{0.7995}{0.1281}$$

or V_r =0.4003. Since for liquid Ar,

$$V_C = \frac{Z_C RT_C}{P_C} = \frac{(0.291)\,(0.0821)\,(150.72)}{48} = 0.0750 \text{ lit}$$

Therefore,

V_0 = (0.4003) (0.0750 lit) = 0.0300 lit

The V_0 values for those liquids listed in Table 2, are calculated in the same way and are given in this table for the isotherm T_r =0.8.

In order to calculate V_r, the molar volume of liquid, which can be calculated by using V=ZRT/P, is divided by V_0. Then the quantity (Z-1) V_r^2 is plotted against $1/V_r^2$ for some different liquids, for the isotherm T_r= 0.8. The results are shown in Figures 7, 8, and 9, in which the lines are almost superimposed. In comparison with Figures 4 through 6, lines in Figures 7, 8, and 9 are much more superimposed, and then the new dimensionless volume (V_r) plays an important role in finding a relatively good universal function for the isotherm T_r = 0.8. Finding a universal function for (Z-1) V_r^2 in terms of $1/V_r^2$ for an isotherm means that Z=Z (V_r, T_r)is a universal function for liquids, and therefore the principle of corresponding states can be applied for liquids without having to use the acentric factor.

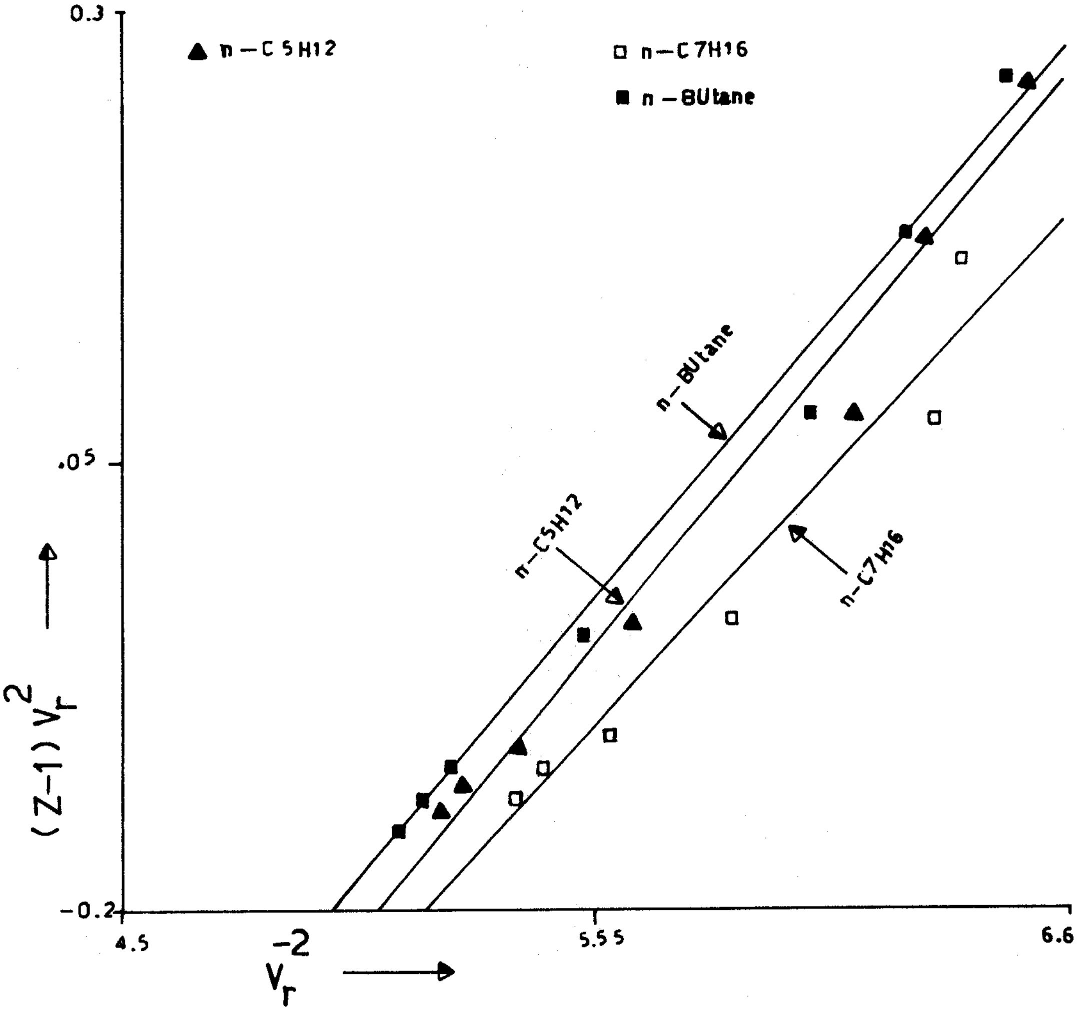

Figure 6. The quantity V_r^2 (Z-1) versus $1/V_r^2$ for three different liquids (T_r=0.8).

Discussion

There are a few points to be discussed here. One point which is based on the Figures 7, 8, and 9, is that if the compressibility factor is expressed in terms of appropriate dimensionless variables, then, the principle of corresponding states works well, and there is no need to introduce additional parameters like the acentric factor. In this work it has been shown that if the compressibility factor, Z, is expressed in terms of T_r and V_r (instead of expressing it in terms of T_r and P_r), the principle of corresponding states works well.

The second point is in regard to the Pitzer et al. [14] statement. They believe that introducing the acentric factor is mainly because of the fact that the sum of the inverse sixth power terms applying to the various portions of a pair of complex molecules cannot be replaced by a single inverse sixth power term in the distance between molecular centers. Even though our calculations are based on the Lennard-Jones (6-12) potential, the resulting equation for Z in terms of P_r and T_r, equation (21), shows that we should not expect to have a universal function for Z; because, in addition to P_r and T_r, Z depends on Z_c, the value of which depends on the specific fluid. The model works well for the small molecules (see Figure 4), and it can still be used for larger molecules, like n-pentane and n-heptane (see Figures 5 and 6). The variances for all lines are of the order of 10^{-5}, see Table 2. Our calculations show that the main reason for having to use the acentric factor as the third variable for the functions Z, Z=Z (T_r, P_r, ω), is due to the fact that P_r is not an appropriate variable for Z. If the new defined

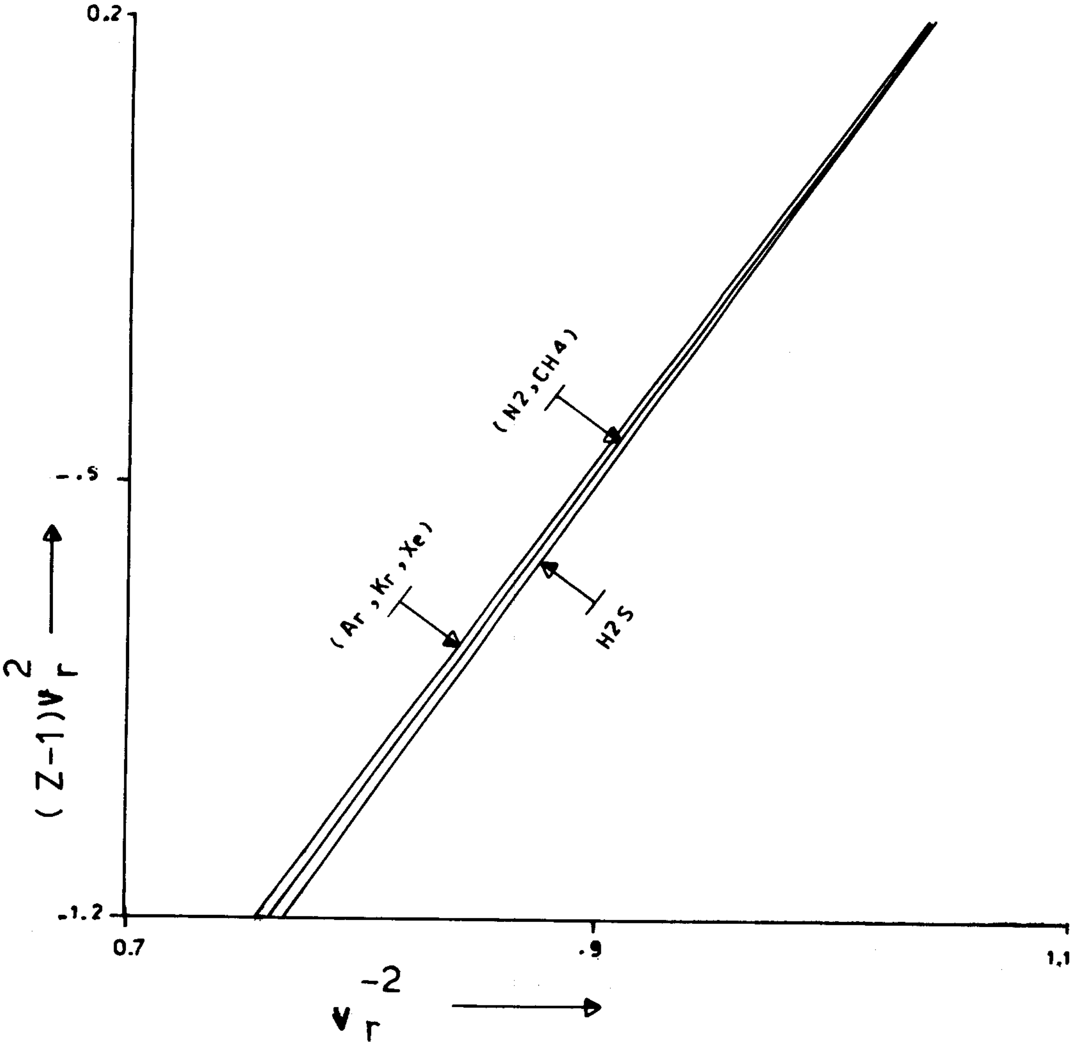

Figure 7. The quantity V_r^2 (Z-1) versus $1/V_r^2$ for six different liquids (T_r=0.8).

dimensionless volume,V_r, is used instead of P_r as a reduced variable for Z, then, this function becomes a relatively good universal function (see Figures 7, 8, and 9), and no additional parameter, like the acentric factor, is needed.

The reason that the lines in Figures 7, 8, and 9 are not completely superimposed may have different origins, such as using the calculated value for V_0 from equation (15), instead of using the actual values; using calculated values for Z from tables in reference [17], rather than using the actual values; and using the Lennard-Jones (6-12) potential for the interaction between two molecules.

The idea of taking the volume into account for the representation of the principle of corresponding states was used by Vetere [17]. He introduced a linear function between Z and P_r for each specific V_r.

A statistical-mechanical theory has recently been presented to derive a new analytical equation of state by Song and Mason [18]. Their approach is quite different from ours however, it is curious that the resulted equation of state is a quintic in the density, just like ours. Their equation of state is more complicated than equation (15) of this work.

One may say that the treatment of volume instead of pressure is more difficult, practically, and in fact this is the major reason that most people use P_r as a variable rather than V_r. This point should not be considered as a disadvantage for our equation of state, because equation (15) may be written as,

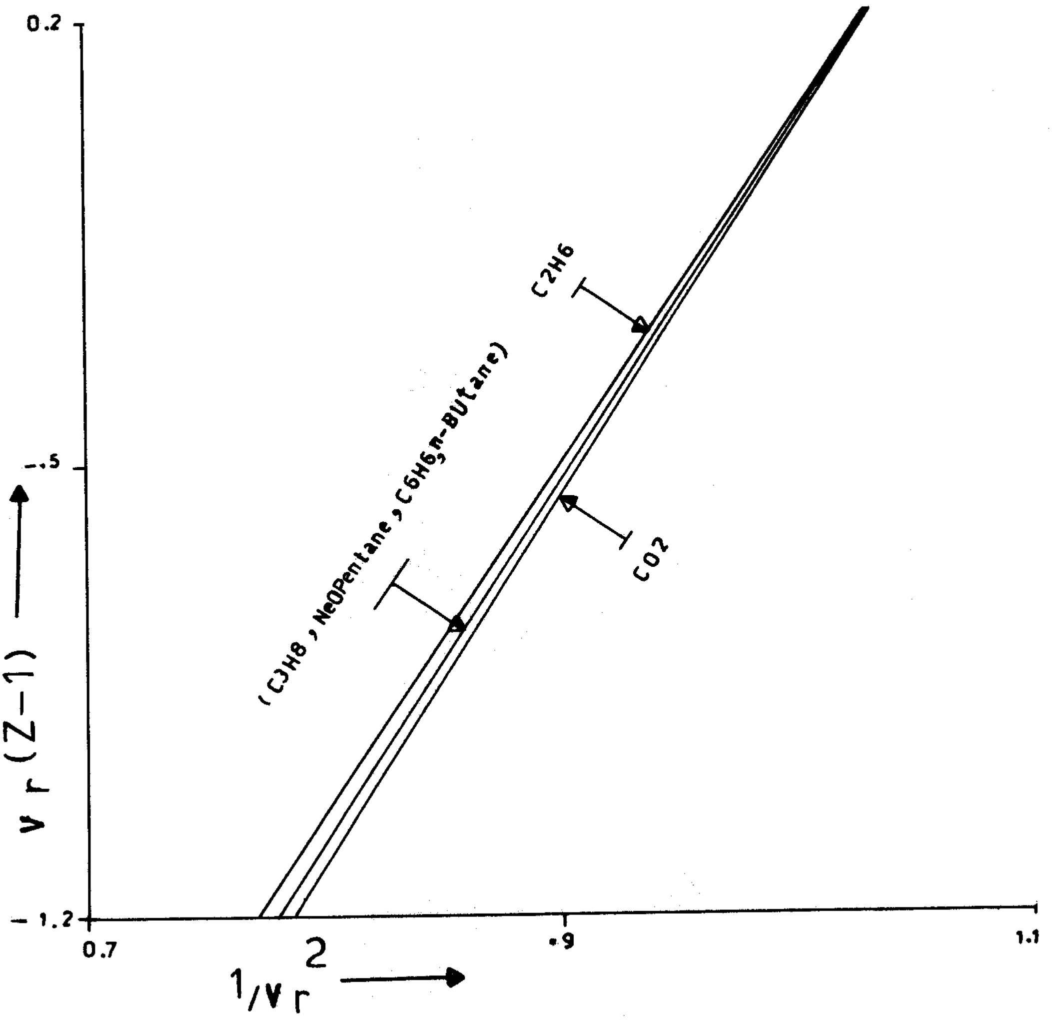

Figure 8. The quantity V_r^2 (Z-1) versus $1/V_r^2$ for six different liquids (T_r=0.8).

$$\frac{Z^2(Z-1)}{P^2} = A'\left(\frac{P^2}{Z^2}\right) - B'$$

(by substituting $V=\frac{ZRT}{P}$ in eq. 15), A' and B' are temperature dependent constants. In this case the function $Z^2(Z-1)/P^2$ against P^2/Z^2 is linear, and if the reference pressure, P_0, is defined in such a way that at Z=1, $P=P_0$, and the reduced pressure is defined as $P_r = P/P_0$, then the lines should be superimposed. This point will be explored in our future publications.

The equation of state given by equation (15) is limited, however, to the liquid phase. This is due to the fact that the contribution of volume change in ΔS is discarded in equation (6). For this reason, the linear functions are not obtained in Fig. 3 (for the gas phase).

If we define ξ (T,V) as,

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\xi\,(T,V)}{V}$$

Then, the equation of state will generally be as,

$$(Z-\xi)\,\frac{1}{V^2} = \frac{A}{V^2} - B$$

which holds for both the gas and the liquid phase. Now the main problem is to find an appropriate function for ξ, in terms of T, and V, A and B in terms of T. This is not done here, but it may be done by using our extended low of corresponding states, which will appear in our future publications.

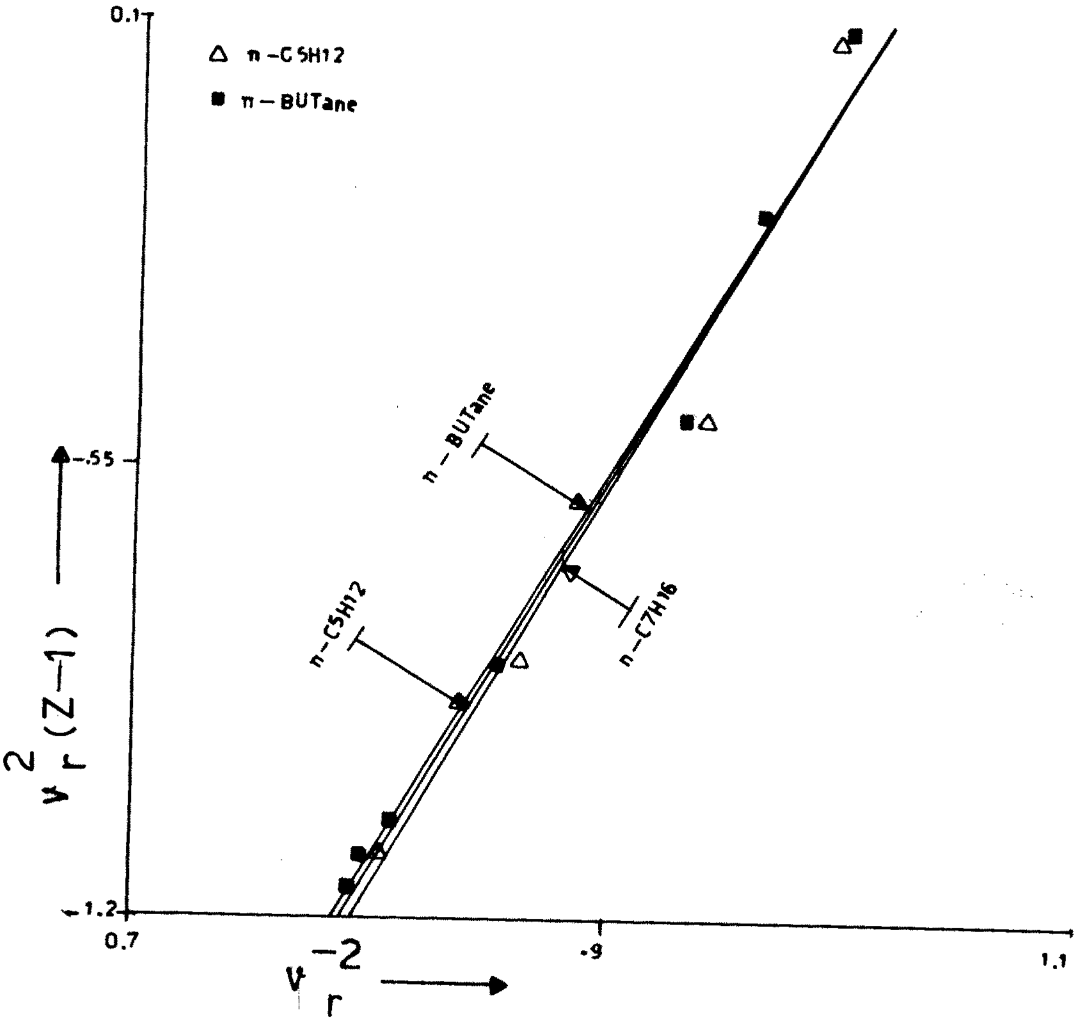

Figure 9. The quantity V_r^2 (Z-1) versus $1/V_r^2$ for three different liquids (T_r=0.8).

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