A NEW TRI-PARAMETRICAL LAW OF CORRESPONDING STATES FOR SUBCRITICAL DENSE FLUIDS

*Parsafar, Gholam Abbas and Ghayeb, Yousef**
Department of Chemistry, Isfahan University of Technology, Zip code 84154, Isfahan, I.R. Iran

ABSTRACT: *This article introduces a new tri-parameter law of corresponding states from the known regularities,namely the LIR and the Zeno line for dense fluids (when $T<0.5T_z=T_c$). Two of these parameters are the Zeno line Parameters and the third parameter (the fluid parameter), has been obtained from the LIR, this parameter is solely dependent upon the fluid characteristics. The third parameter can be obtaind from p-v-T data of at least two different isotherms of the fluid. These three parameters enable us to calculate quantities such as the density of the fluid, within a reasonable accuracy (the maximum error is less than 5%). Comparing the calculated results with the experimental values shows that this law can at least be applied to spherical, polar and hydrocarbon fluids.*

KEY WORDS: *Corresponding states, Supercritical, Dense fluid, Fluid parameter.*

INTRODUCTION

The linear isothermal regularity or simply LIR was introduced for dense fluids by *Parsafar* and *Mason* [1,2]. According to this regularity, for each isotherm, $(Z-1)v^2$ is linear in terms of ρ^2 as,

$$(Z-1)v^2 = A + B\rho^2 \qquad (1)$$

where $\rho=1/v$ is the molar density and Z is the compression factor. Experimentally, it was found that LIR is valid for nonpolar, spherical, linear, polar and quantum fluids, and also fluid mixtures [3]. The LIR is valid for densities greater than the Boyle density ρ_B and temperatures below twice of the Boyle temperature. The parameters A and B depend upon the molecular characteristics of the fluid and temperature. The temperature dependence of A and B are given as,

$$A=A_2-\frac{A_1}{RT}\ ,\ B=\frac{B_1}{RT}$$

The parameter A_1 and B_1 are related to the intermolecular attractions and repulsions respectively and A_2 is related to the non-ideal contribution of the thermal pressure. The LIR has been used to predict many empirically known regularities and also some new ones [4,5].

* *To whom correspondence should be addressed.*
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It has been empirically observed that T is linearly dependent upon ρ if Z=1. This regularity has been empirically observed and reported for different fluids like N_2 , O_2 ,CH_4 and C_2H_6 [6]. The correlation coefficient observed for the plot of T versus ρ is approximately 0.999 and the linearity is given by ;

$$\frac{T_{zl}}{T_z} + \frac{\rho_{zl}}{\rho_z} = 1 \qquad (2)$$

where T_{zl} and ρ_{zl} are the temperature and density lying on the Zeno Line, respectively, while T_z and ρ_z are the intercept with the T and ρ axes, respectively.

Tri-parameter law of corresponding states

The LIR regularity can predict the point lying upon the Zeno line . The LIR can actually predict the points of the Zeno line in which the temperature is low and the density is high or to be more exact when $T<0.5T_z$ and $\rho>0.5\rho_z$. Using the LIR , we can calculate the Zeno line density at any temperature from the following equation .

$$\rho_{zl}^2 = -\frac{A}{B} \qquad (3)$$

If the density is reduced by ρ_{zl}, the reduced LIR equation of state is given as ,

$$(Z-1)(\frac{v}{v_{zl}})^2 = A_r + B_r (\frac{\rho}{\rho_{zl}})^2 \qquad (4)$$

(Note that ρ_{zl} is the density of the fluid at temperature when Z=1)

Eq.(4), which is the reduced form of the LIR will be denoted as RLIR from now on. Eq.(1) may be written as,

$$(Z-1)\, v_r^2 = A\,\rho_{zl}^2 + B\,\rho_{zl}^4\rho_r^2 \qquad (5)$$

where $v_r = 1/\rho_r = v/v_{zl}$. Comparing Eq. (4) with Eq. (5), we find

$$A_r = A\,\rho_{zl}^2 \qquad (6a)$$

and

$$B_r = B\,\rho_{zl}^4 \qquad (6b)$$

Substitution of ρ_{zl} from Eq.(3) into Eqs.(6a) and (6b) gives the following result:

$$B_r = -A_r = \frac{A^2}{B} \qquad (7)$$

Therefore if $(Z-1)v_r^2$ is plotted versus ρ_r^2 both the slope and intercept of the resulting line have the same absolute value. If we solve Eq.(2) for ρ_{zl} [$\rho_{zl} = (1- T_{zl}/T_z)\,\rho_z$] and insert it into Eq.(6b) the following result will be obtained.

$$B_r = B\ (1-T_r)^4\,\rho_z^4 \qquad (8)$$

in which T_r is the reduced temperature, defined as $T_r=T_{zl}/T_z$. If $B=B_1/RT$, $T_{zl}=T_rT_z$ are substitued into Eq. (8), the following relation results (Note that T and T_{zl} are the same),

$$B_r = \frac{B_1}{RT_rT_z}(1-T_r)^4\rho_z^4 \qquad (9)$$

Eq. (9) can be used to obtain the slope of the RLIR line, if the reduced temperature, T_r and the parameters of the Zeno line , T_z and ρ_z are available. The ratio of the slopes of the RLIR lines for any two fluids at the same T_r is ,

$$\frac{B_{r,i}}{B_{r,j}} = \frac{B_{1,i}}{B_{1,j}}\,\frac{T_{z,j}}{T_{z,i}}\,[\frac{\rho_{z,i}}{\rho_{z,j}}]^4 \qquad (10)$$

Eq. (10) is a magnificient achievement, that is the ratio becomes a constant , of course, if the temperature is reduced by T_z . The value of this ratio is independent of density and temperature , and is soley dependent on the characteristic of the two fluids . In such a case , if we choose a reference fluid we can calculate the ratio for any other fluid. We shall refer to this ratio as the "fluid parameter" and It will be denoted By Φ . Argon has been chosen as a reference fluid. Therefore;

$$\Phi_j = \frac{B_{r,i}}{B_{r,Ar}} \qquad (11)$$

The value of the fluid parameter will be calculated in the next section by using the experimental p-v-T data for different fluids.

Calculation of fluid parameter

Using p-v-T experimental data for Ar [7], we can calculate the value of B_r at any given temperature by using Eq.(7). For this purpose, we may plot $(Z-1)v^2$ versus ρ^2 for any isotherm of argon, from which the values of the slope and intercept can be obtained for

Table 1: The slope,B, and Intercept , A, of the LIR and the value of B_r calculated from Eq.(7) for Ar at given temperatures (the experimental data are taken from Ref.7)

T(K)	A × 10^6 (L^2 mol^{-2})	B × 10^8 (L^4 mol^{-4})	B_r
90	−8813(0.103)	672(0.110)	11.5564(0.317)
95	−8090(0.295)	637(0.311)	10.2768(0.901)
100	−7406(0.390)	602(0.409)	9.1136(1.188)
110	−6168(0.412)	534(0.442)	7.1290(1.266)
120	−5118(0.411)	479(0.455)	5.6172(1.278)
130	−4416(0.361)	436(0.416)	4.4700(1.139)
140	−3848(0.192)	408(0.225)	3.6263(0.608)
150	−3435(0.497)	393(0.575)	3.0025(1.568)
160	−3025(0.483)	374(0.520)	2.4453(1.486)
170	−2693(0.703)	361(0.742)	2.0068(2.148)
180	−2336(0.566)	341(0.535)	1.6007(1.667)
190	−2009(0.342)	321(0.290)	1.2573(0.9739)
200	−1749(0.462)	307(0.366)	0.9955(1.290)

The figure in the parantheses denotes absolute percent deviation.

that isotherm. The calculated values of B_r are given in Table 1 for Ar at some known temperatures.

Similar calculations are done for N_2 fluid using the p-v-T data given in Ref. 7, for which the results are given in Table 2. Using the calculated values of B_r given in Tables 1 and 2 along with Eq.(11), we are able to calculate the fluid parameter for nitrogen at different temperatures. The results are presented in Fig. 1. A glance at this figure shows that at $T>0.5\ T_z$ the fluid parameter changes very rapidly with temperature, so that it is impossible to assign a constant value to it. However at $T<0.5\ T_z$ the fluid parameter has a small fluctuation around $\Phi(N_2)=1.235$,Such a behavior is expected (section 2). A similar behavior is observed at least for the fluids given in Table 3, for which the calculated fluid parameters are tabulated .

Calculation of density

A wide renge of p-v-T data has been reported in literature for Ar, from which the parameters A and B of the LIR equation of state can easily be calculated for reference fluid (Ar). Due to the fact that the

Table 2: Same as Table 1 for N_2 (the experimental data are taken from Ref. 7).

T(K)	A × 10^6 (L^2 mol^{-2})	B × 10^8 (L^4 mol^{-4})	B_r
80	−12730(0.292)	143(0.301)	11.3322(0.885)
95	−9119(0.102)	116(0.102)	7.1689(0.311)
100	−8206(0.094)	109(0.094)	6.1780(0.287)
115	−6111(0.094)	92(0.093)	4.0625(0.288)
120	−5592(0.068)	88(0.073)	3.5539(0.208)
135	−4350(0.311)	79(0.248)	2.3953(0.870)

temperature dependence of the A and B parameters are known, see section 1, the values of the parameters can easily be calculated at other temperatures. Having the values of A and B at only two different temperatures for a fluid, is enough to calculate their values at any other temperature for that fluid .

In case the data for two isotherms are not available , we need the values of the fluid parameter, the parameters of the Zeno line , along with the p-v data of argon at that (reduced) temperature, to calculate the values of the A and B parameters and then density of fluid at that temperature in any given pressure. In order to carry out such a calculation , we first use the experimental p-v-T data of Ar to calculate the B_r for the reference fluid by Eq.(7) and then Eq.(11) can be used to calculate B_r of the fluid.

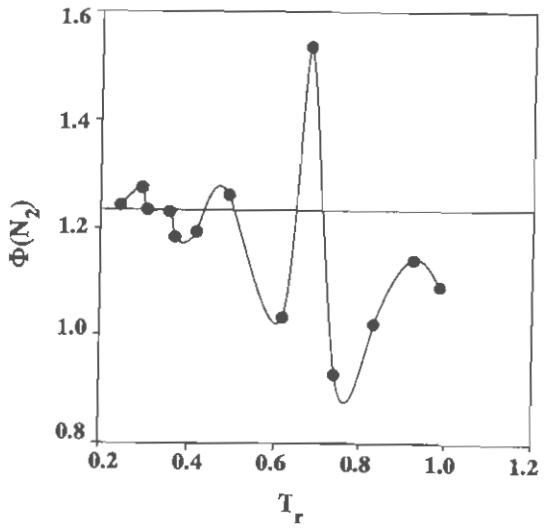

Fig. 1. Fluid parameter of N_2 as a function of reduced temperature , $T_r = T/T_z$

Table 3 : The parameters of the LIR and the fluid parameter, Φ ,for given fluids (all experimental data ara taken from Ref. 7).

Fluid	A_1/R ($L^2\ mol^{-2}\ K$)	A_2 ($L^2\ mol^{-2}$)	B_1/R ($L^4\ mol^{-4}\ K$)	Φ
N_2	1.5708(3.081)	0.007289(6.07)	0.0012742(2.95)	1.2351(3.02)
O_2	1.3368(3.183)	0.005166(6.18)	0.0007018(3.96)	1.0973(6.88)
Xe	4.4206(1.895)	0.007857(3.58)	0.0057301(4.72)	0.9812(5.25)
CH_4	2.4334(3.738)	0.006786(7.38)	0.0021402(8.43)	1.068(3.71)
CO_2	4.9000(.1498)	0.011000(0.218)	0.0010491(36.3)	1.848(6.63)
C_3H_8	22.019(4.165)	0.032519(7.78)	0.0680854(9.32)	1.5573(11.2)
C_4H_{10}	66.679(7.262)	0.131066(11.0)	0.4948500(8.38)	1.6111(4.41)
C_5H_{12}	97.447(0.8444)	0.153920(3.91)	0.7866930(0.590)	1.70930(3.55)

The figure in the parantheses denotes the maximum of the absolute percent deviation .

Finally, Eqs.(2) , (3) and (7) can be simultaneously used to obtain the values of A and B at the given temperature, by which the density can be calculated using the LIR. The calculation was done for N_2 and the results are compared with the experimental data in Fig. 2. The results for other fluids are summerized in Table 4.

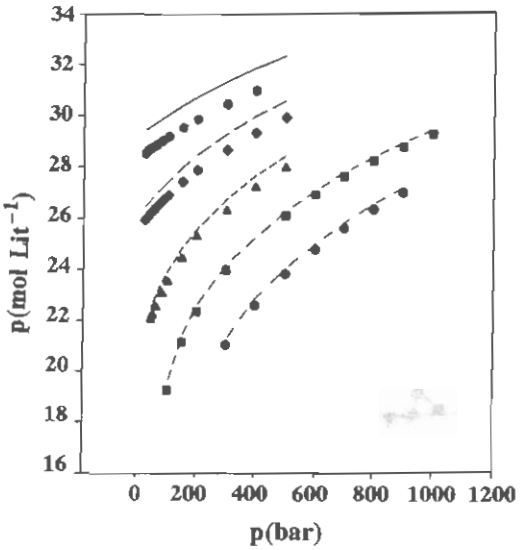

Fig. 2. The calculated densities of N_2 versus pressure, compare to those of experiment, for 160 K(●) , 135K(■), 115K (▲), 95 (◆) and 80K(●) isotherms.(Note that the maximum deviations are due to the lowest isotherm which is less than 4.2 percent.)

Summary and conclusions

A tri-parameter law of corresponding states for dense fluid has been derived on the basis of the LIR and the Zeno line , which is valid for $T<0.5T_z$ and $\rho>0.5\rho_z$, i.e. the subcritical region . Two of the three parameters are due to the Zeno line and the third , the fluid parameter, is also dependent on the parameters of LIR. It is shown that the fluid parameter depends only on the kind of the fluid and the reference fluid, Eq.(10). Therefore ,it is possible to calculate the density of any fluid (at any given temperature and pressure) for which these three parameters are known.

Table 4: The calculated density for different substances for given temperature range ,ΔT, and the pressure range ,ΔP, the maximum absolut percent deviation of the calculated density , 100 $(\Delta\rho/\rho)_{max}$ is also given.

Substance	ΔT(K)	p(bar)	$100(\Delta\rho/\rho)$max
N_2	80-160	25-1000	4.17
O_2	90-200	45-1000	1.09
Xe	290-350	200-800	4.32
CH_4	150-240	50-1000	1.04
CO_2	280-350	120-600	4.2
C_2H_6	200-300	80-700	2.53
C_3H_8	250-440	90-600	0.97
C_4H_{10}	293-393	10-200	1.9
C_5H_{12}	293-393	20-200	2.04

Comparing with the experimental data the calcu-

lated density has a maximum deviation of less than five percent in a wide pressure range of 1000 bar, (Table 5). Due to the fact that the composition dependency of the A and B parameters of LIR are already known[3], it is possible to apply the tri-parametrical law of corresponding states to mixtures, as well, if the composition depedencies of the Zeno line parameters can also be obtained. This task remains for the future.

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