

## **Linear Isotherm for Compressed Molten Alkali Metals**

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*Received September 17, 1997*

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Molten alkali metals are shown to be in the domain of the newly developed linear regularity that is valid for pure compressed liquids and liquid mixtures. It holds in the range of melting to boiling temperature and shows deviations as the critical temperature is approached. The agreement with experimental data is better than 1.4% when it is used to predict the density of molten Li, Na, K, Rb, and Cs metals. A reasonable conformity with the ISM statistical mechanical equation of state is manifested.

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**KEY WORDS:** alkali metals; density; equation of state; linear regularity.

### **1. INTRODUCTION**

The recently developed linear isotherm regularity (LIR) for dense fluids is attractive for both practical purposes and for theoretical investigations [1, 2]. This feature may be considered similar to that of the other thermodynamic regularities such as, (i) pressure versus temperature at constant density  $\rho$  [3], (ii) linearity of a Clausius–Clapeyron plot [4], (iii) linearity of rectilinear density diameter [5], and (iv) the common bulk modulus point for compressed liquids [6–8], to mention a few.

The LIR equation of state suggests that  $(Z - 1)v^2$  versus  $\rho^2$  is linear for a dense fluid and valid for atomic, polar, nonpolar molecular systems, liquid mixtures [2], and quantum fluids, where  $Z = p/\rho kT$  is the compressibility factor,  $v$  is the molar volume of fluid, and  $\rho = 1/v$  is the molar density [1, 2]. The range of applicability for densities  $\rho$  is larger than the Boyle density  $\rho_B$ , valid up to the freezing line for liquids, and up to twice

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$\rho_B$  for supercritical fluids. The LIR linear parameters, the intercept, and the slope depend on the temperature and are related to the intermolecular repulsive and attractive forces. At the intermediate intermolecular separation the attractive and repulsive forces are balanced, leading to the feature of linearity. It is valid for temperatures below the Boyle temperature  $T_B$  in the liquid state and below twice  $T_B$  for supercritical fluids.

LIR applies to fluids consisting of a wide range of simple dipolar molecules, besides atomic and molecular ones, motivating us to search for its consequences in complex cases. The purpose of this paper is to explore its range of validity for molten alkali metals, which are typical complex and interesting liquid systems with important industrial applications.

Although alkali metals contain special properties that affect their thermodynamic behavior, it appears that they show regularity cases (i)–(iii), mentioned above. The main difficulty in the theoretical treatment of alkali metals is the difference in the nature of the intermolecular forces in the liquid and the gaseous states due to special associative interactions leading to polyatom formation in gaseous states [9, 10]. Moreover, two singlet- and triplet-type intermolecular potentials arise from the spin coupling of the two single-valence electrons of the associating partners, making the investigation more complicated even in the ideal low-pressure limit.

In spite of the difficulties mentioned above, it has been shown that the Ihm–Song–Mason (ISM) analytical equation of state is quite applicable to molten alkali metals [11].

## 2. LINEAR ISOTHERM REGULARITY

The basic structure of the LIR equation of state is based on thermodynamic arguments and reads, in its modified simple form, as [1]

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

where  $Z$ ,  $v$ , and  $\rho$  have their usual meanings. The intercept,  $A$ , and the slope,  $B$ , in Eq. (1) are two system-dependent constants, which vary with temperature, and the thermodynamic equation of state plus inverse power laws for the pair potential interaction have been used to show a temperature dependence in the form of

$$A = A_2 - A_1/RT \quad (2)$$

and

$$B = B_1/RT \quad (3)$$

In Eqs. (2) and (3),  $A_1$  and  $B_1$  are constants related to the intermolecular attraction and repulsion, respectively, while  $A_2$  is related to the nonideal contribution to the thermal pressure.

It has been shown that Eq. (1) can be used to demonstrate the law of corresponding states as  $Z = Z(T_r, P_r, Z_c)$ , where  $Z_c$  is the compressibility factor at the critical point, and  $T_r$  and  $P_r$  are the reduced temperature and the reduced pressure, respectively [12]. Since  $Z_c$  depends on a particular system, the universality could not be established perfectly. It has been suggested that the establishment of a reference state (at which the volume shall be reduced) that is similar for interaction of two neighboring molecules in all liquids improves the universality feature. In this regard some progress has been made [12].

### 3. EQUATION OF STATE FOR COMPARISON

We compare and check the range of validity of the linear regularity isotherm with the ISM analytical equation of state [13, 14]. The ISM equation of state is based on statistical mechanics and is known for its accuracy in the subcritical and supercritical regions including the compressed liquid state [15]. The LIR version of the ISM equation of state is

$$(Z-1)v^2 = \frac{1}{\rho} \left( \frac{B_2 - \alpha}{1 + \delta b \rho} + \frac{\alpha}{1 - \lambda b \rho} \right) \quad (4)$$

where  $B_2$ ,  $\alpha$ , and  $b$  are three temperature-dependent constants characteristic for the particular system. Of the three constants,  $B_2$ , the second virial coefficient, has the central role that represents an effective intermolecular interaction, and  $\alpha$  scales for the softness of the repulsive forces and is equal to the contribution of the repulsive side of the potential function to the second virial coefficient;  $b$  is an analogue of the van der Waals covolume that is related to  $\alpha$  by  $b = d(\alpha T)/dT$ . The constants  $\delta$  and  $\lambda$  are characteristics of a particular fluid, but  $\delta$  is only a small correction for some secondary effects of the attractive forces and can be taken to be equal to  $0.22\lambda$  for practical purposes. The constant  $\lambda$  is equal to 0.454 for noble gases and, in general, can be calculated by successive approximation with the aid of Eq. (4) [14]. When the details of the pair potential function are known,  $B_2$ ,  $\alpha$ , and  $b$  can be calculated by integration [13]. Other methods, which involve calculation of  $B_2$  from correlations and the use of thermodynamic functions as scaling parameters for the calculation of  $\alpha$  and  $b$ , are available [11, 16, 17].

#### 4. RESULTS FOR ALKALI METALS

In employing Eq. (1) for alkali metals, we first examine the linearity feature by presenting their volumetric behavior at various temperatures. Figures 1–5 show the results at three temperatures, 600, 1000, and 1600 K for Li, Na, K, Rb, and Cs, respectively. It can be seen that over the entire range of pressures, from 100 to 1000 atm, the variations are linear as in other dense fluids. In the  $p$ - $T$  plane, the isochores are straight lines. Measurements [18–22] reproduce the  $p$ - $v$ - $T$  data within the experimental error. Moreover, it is consistent with a hard-sphere equation of state approach [23].

The results for the alkali metals (Li through Cs) including the slopes and intercepts at various temperatures are shown in Table I. Since both  $(Z-1)v^2$  and  $\rho^2$  are subject to experimental uncertainties, we have also reported the square of the linear correlation coefficient of the linear fit of the experimental data to the Eq. (1). If the square of the linear correlation coefficient,  $R^2$ , is within 0.005 of unity, the fit is considered to be good [24]. For all cases in Table I, the deviations of the calculated densities are within 1.4% of the experimental data. Since both  $A$  and  $B$  are temperature dependent, we have tabulated the results for Cs as a typical metal of alkalis at various temperatures. (See Table II.)

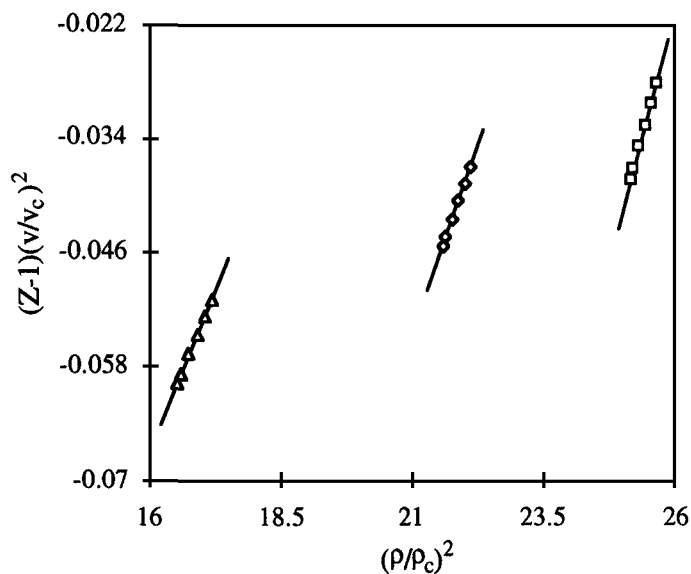


Fig. 1.  $(Z-1)(v/v_c)^2$  versus  $(\rho/\rho_c)^2$  for Li at 600 K ( $\square$ ), 1000 K ( $\diamond$ ), and at 1600 ( $\triangle$ ).

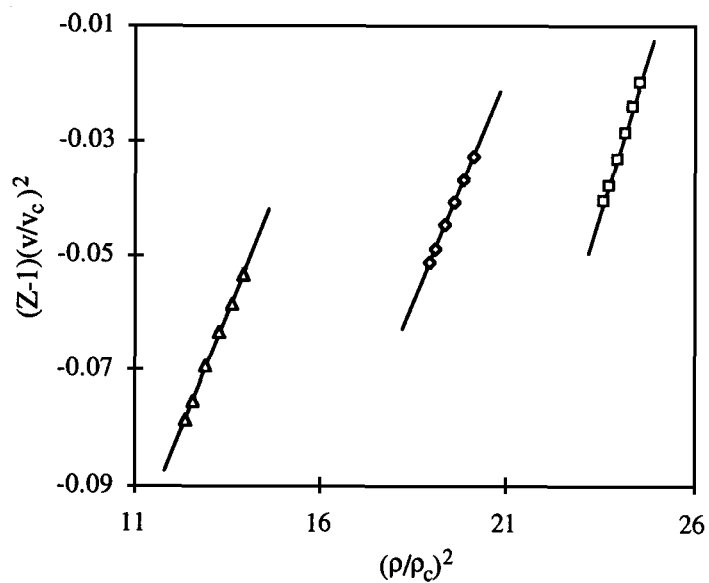


Fig. 2. The same as Fig. 1 for Na.

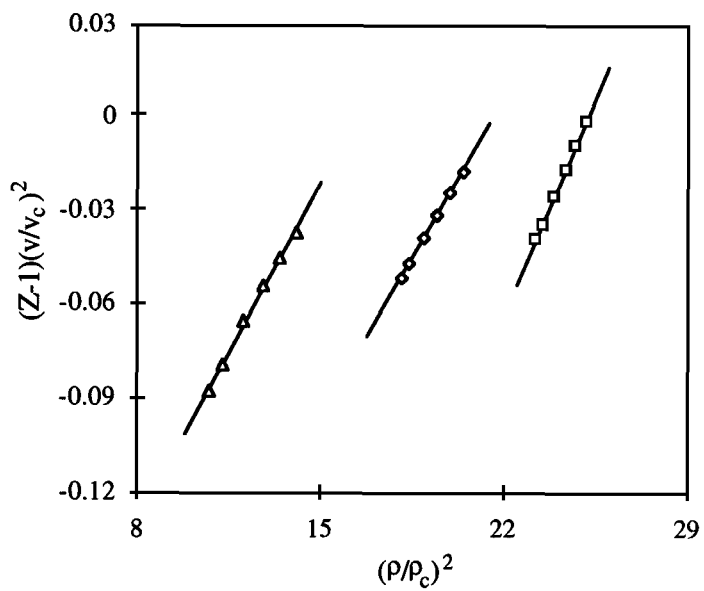


Fig. 3. The same as Fig. 1 for K.

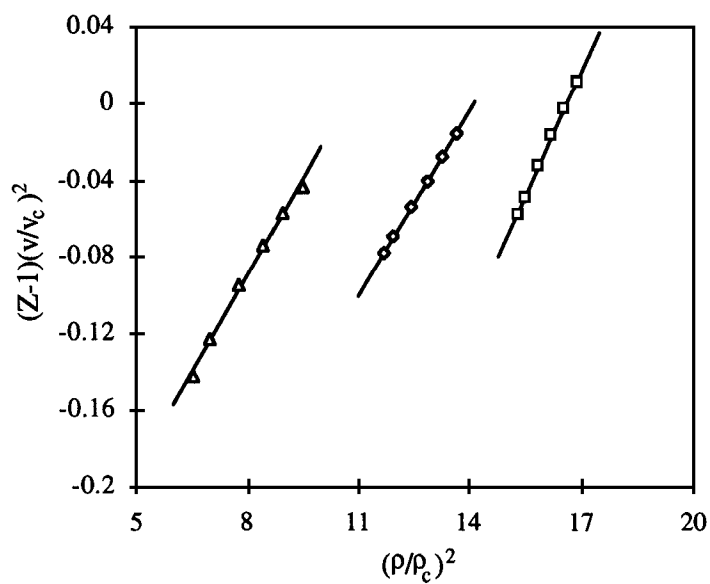


Fig. 4. The same as Fig. 1 for Rb.

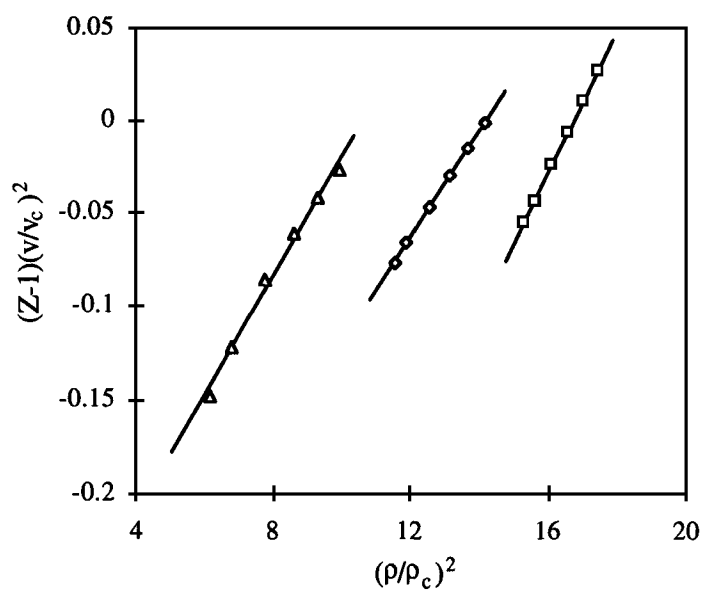


Fig. 5. The same as Fig. 1 for Cs.

**Table I.** The Reduced Intercept ( $A$ ) and Slope ( $B$ ) of Eq. (1) at Three Temperatures for Li, Na, K, Rb, and Cs<sup>a</sup>

|    | $T$ (K) | $A$     | $B$     | $R^2$  | $\Delta p$ (bar) | $(\text{Dev})_p$ (%) <sup>b</sup> |
|----|---------|---------|---------|--------|------------------|-----------------------------------|
| Li | 600     | -0.5721 | 0.0212  | 1.0000 | 100-1000         | 0.002 (0.004)                     |
|    | 1000    | -0.3756 | 0.0153  | 1.0000 | 100-1000         | 0.002 (0.003)                     |
|    | 1600    | -0.2831 | 0.0136  | 1.0000 | 100-1000         | 0.004 (0.007)                     |
| Na | 600     | -0.5548 | 0.0217  | 0.9998 | 100-1000         | 0.003 (0.004)                     |
|    | 1000    | -0.3546 | 0.0160  | 1.0001 | 100-1000         | 0.007 (0.02)                      |
|    | 1600    | -0.2794 | 0.0163  | 0.9990 | 100-1000         | 0.051 (0.06)                      |
| K  | 600     | -0.5058 | 0.0201  | 1.0000 | 100-1000         | 0.006 (0.009)                     |
|    | 1000    | -0.3146 | 0.0146  | 0.9999 | 100-1000         | 0.032 (0.05)                      |
|    | 1600    | -0.2536 | 0.0155  | 0.9969 | 100-1000         | 0.234 (0.39)                      |
| Rb | 600     | -0.7184 | 0.0432  | 0.9997 | 100-1000         | 0.011 (0.017)                     |
|    | 1000    | -0.4477 | 0.03161 | 0.9995 | 100-1000         | 0.046 (0.072)                     |
|    | 1600    | -0.3584 | 0.03357 | 0.9959 | 100-1000         | 0.371 (0.68)                      |
| Cs | 600     | -0.6462 | 0.03855 | 1.0000 | 100-1000         | 0.017 (0.027)                     |
|    | 1000    | -0.4042 | 0.02842 | 0.9990 | 100-1000         | 0.083 (0.14)                      |
|    | 1600    | -0.3360 | 0.03156 | 0.9914 | 100-1000         | 0.701 (1.41)                      |

<sup>a</sup> Also listed are the square of the linear correlation coefficient ( $R^2$ ), the pressure range ( $\Delta p$ ), and the average absolute percentage deviation of the calculated density [ $(\text{Dev})_p$ ].

<sup>b</sup> The data in parentheses are maximum deviations.

**Table II.** The Same as Table I but for Cs at Different Temperatures<sup>a</sup>

| $T$ (K) | $A$     | $B$    | $R^2$  | $\Delta p$ (bar) | $(\text{Dev})_p$ (%) <sup>b</sup> |
|---------|---------|--------|--------|------------------|-----------------------------------|
| 400     | -0.9379 | 0.0514 | 0.9997 | 50-600           | 0.033 (0.052)                     |
| 500     | -0.7454 | 0.0426 | 0.9998 | 50-600           | 0.027 (0.049)                     |
| 600     | -0.6283 | 0.0375 | 0.9993 | 50-600           | 0.037 (0.058)                     |
| 700     | -0.5477 | 0.0341 | 0.9993 | 50-600           | 0.028 (0.053)                     |
| 800     | -0.5015 | 0.0327 | 0.9987 | 50-600           | 0.068 (0.010)                     |
| 900     | -0.4654 | 0.0318 | 0.9979 | 50-600           | 0.085 (0.012)                     |
| 1000    | -0.4358 | 0.0312 | 0.9971 | 50-600           | 0.121 (0.170)                     |
| 1100    | -0.4104 | 0.0309 | 0.9962 | 50-600           | 0.160 (0.230)                     |
| 1200    | -0.3916 | 0.0310 | 0.9961 | 50-600           | 0.183 (0.270)                     |
| 1300    | -0.3781 | 0.0315 | 0.9956 | 50-600           | 0.230 (0.330)                     |
| 1400    | -0.3700 | 0.0326 | 0.9961 | 50-600           | 0.260 (0.400)                     |
| 1500    | -0.3680 | 0.0343 | 0.9943 | 50-600           | 0.381 (0.560)                     |
| 1600    | -0.3743 | 0.0373 | 0.9916 | 50-600           | 0.573 (0.970)                     |

<sup>a</sup> Updated data from Ref. 27.

<sup>b</sup> The data in parentheses are maximum deviations.

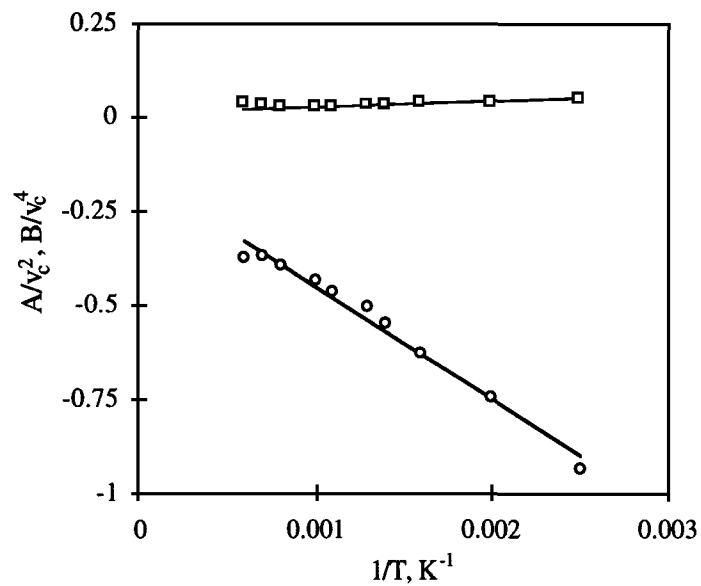


Fig. 6. Variation of the intercept,  $A$  ( $\circ$ ), and the slope,  $B$  ( $\square$ ), with  $1/T$ .

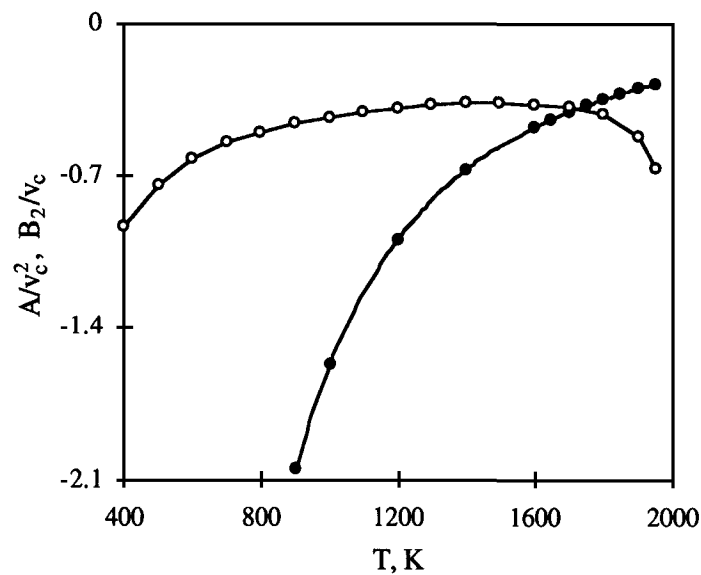


Fig. 7. Variation of the intercept,  $A$  ( $\circ$ ), and the second virial coefficient,  $B_2$  ( $\bullet$ ), with  $T$ .



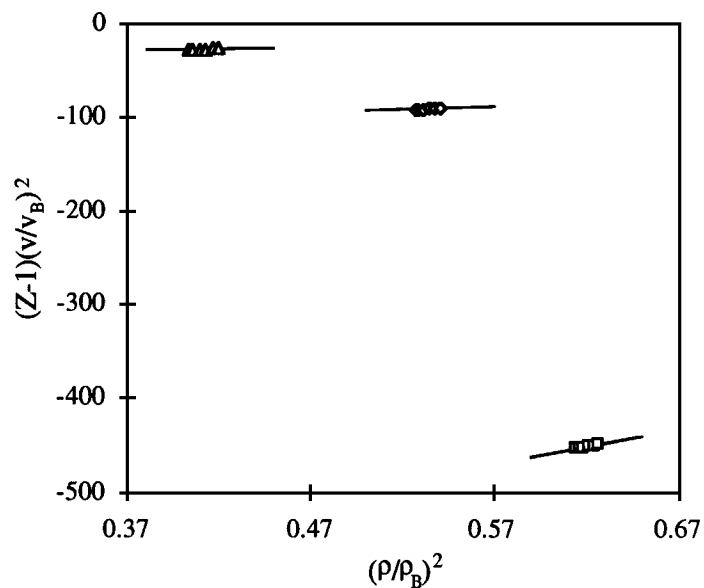


Fig. 8. The isotherms of  $(Z-1)(v/v_B)^2$  versus  $(\rho/\rho_B)^2$  of the LIR version of the ISM equation of state for Li. Also shown are the regions of linearity at 600 K ( $\square$ ), 1000 K ( $\diamond$ ), and 1600 K ( $\triangle$ ).

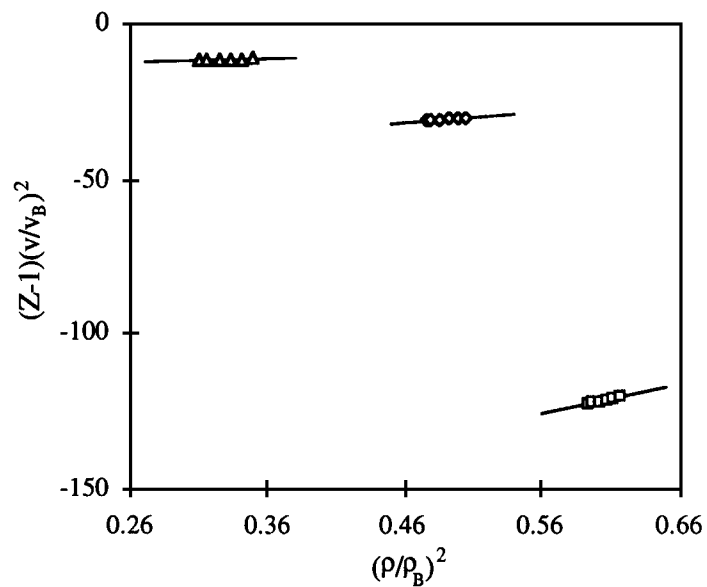


Fig. 9. The same as Fig. 8, for Na.

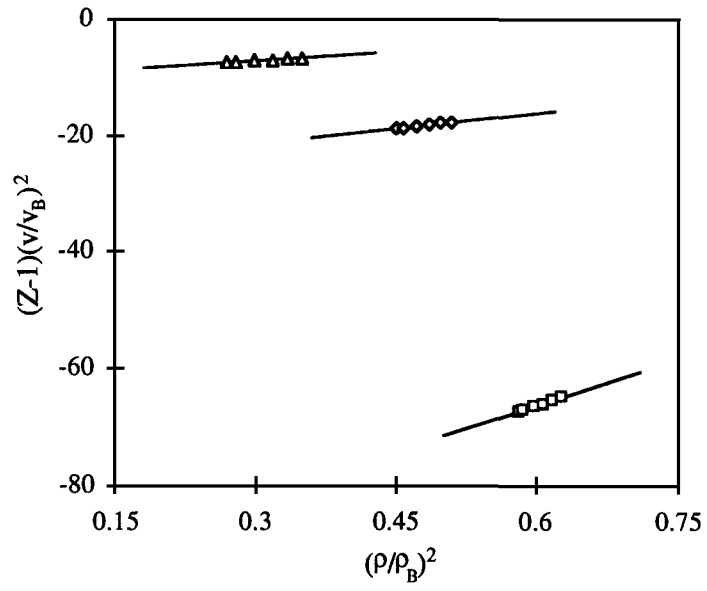


Fig. 10. The same as Fig. 8, for K.

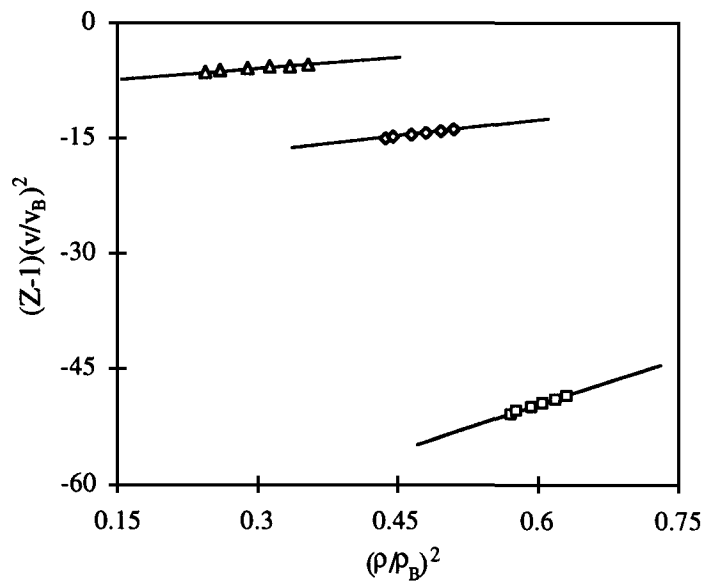


Fig. 11. The same as Fig. 8, for Rb.

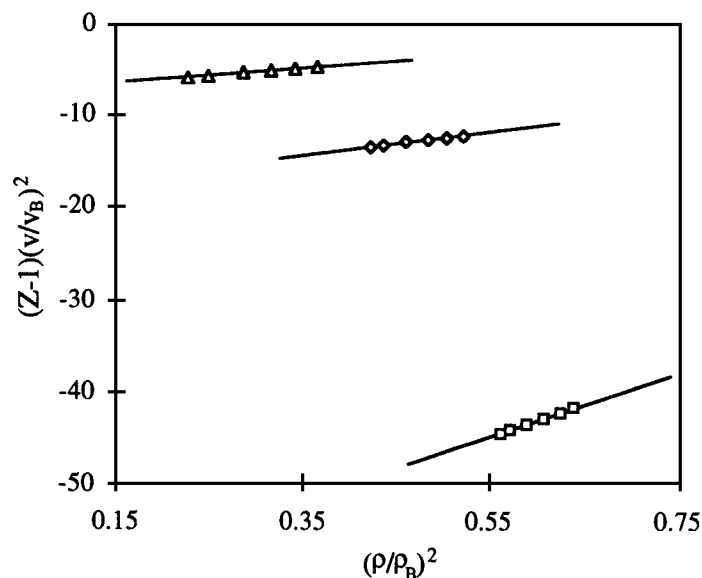


Fig. 12. The same as Fig. 8, for Cs.

Both the intercept,  $A$ , and the slope,  $B$ , have been predicted to be linear in  $1/T$ . This feature is well applied to alkali metals, as shown in Fig. 6, typically for Cs.

The characteristic of the regularity that has been worked out theoretically for nonmetallic fluids is the temperature dependency of  $A$  and  $B$ . This observation applies also in the case of the alkali metals as can be seen from the results for Cs shown in Table II; the variation of  $A$  with temperature is similar to the variation of the second virial coefficient. (See Fig. 7.)

Equation (4) demonstrates the LIR version of the ISM equation of state. Obviously, the right-hand side of this equation is not a function of  $\rho^2$ , but it conforms to the LIR equation of state if it is plotted against  $(\rho/\rho_B)^2$ , and hence, one expects an appreciable linear range. The conformities to the LIR are shown in Figs. 8–12 for Li, Na, K, Rb, and Cs, respectively.

## 5. DISCUSSION

Data for the compressibility factor of molten alkali metals are more limited than for other fluids, but the available data in the pressure range of 50–600 atm nicely demonstrate the linearity, as has already been demonstrated for other fluids. The coefficients  $A$  and  $B$  for alkali metals

vary with temperature as they do for other fluids. However, their values for the alkali metals are smaller by about an order of magnitude.

It has been shown that  $A$  (for nonmetallic liquids) varies with temperature as much as  $B_2$ , the second virial coefficient, does [1]. In the case of alkali metals, this similarity needs further refinements. We recall that the second virial coefficient data for alkali metals are not available at high temperatures, so that the Boyle temperature cannot be determined in practice. In other words, a plot of  $B_2$  versus temperature does not cross the zero line, and thus one practical way for determining the Boyle temperature is by estimation, such as calculating  $B_2$  as a function of temperature from a potential function. A method for the calculation of  $B_2$  as a function of temperature for alkali metals that includes  $B_2^{(1)}$  and  $B_2^{(3)}$  from singlet [superscript (1)]- and triplet [superscript (3)]-type potential interactions, respectively, has been reported in the literature [25]. Of the two model potential functions used in these calculations, the Morse function has been reported as the more reliable. As a result of this calculation,  $B_2^{(1)}$  and  $B_2^{(3)}$  vary with temperature in the opposite manner; at high temperatures, the variations of  $B_2^{(1)}$  go through a maximum in the negative region, without crossing the zero line. When the statistical weighting of singlet and triplet states is applied, the overall variation of  $B_2$  with temperature looks just as normal as that for other fluids [25]. Thermodynamically, however, the singlet state of the alkali metals at high temperatures is the predominant state, whereas the triplet state is the lesser one due to its repulsive nature. Therefore, at high temperatures one may expect  $B_2$  to be dominated energetically by the singlet behavior.

The above arguments, considering pair interactions, are valid for the vapor state. However, in this work we have used the LIR for the liquid state. We have observed that (Fig. 7) the  $A$  values vary with temperature as the  $B_2$  values but go through a maximum in the negative region without crossing the zero line. At present, it is not possible to relate  $A$  to any fundamental physical property directly. However, as the temperature increases, an intrinsic transition in the intermolecular forces of the liquid alkali metals occurs, leading to polyatom formation. Therefore, as the temperature increases, a basic assumption in the derivation of the LIR equation of state (e.g., the nearest-neighboring structure of the liquid state) becomes invalid [12]. Such a consideration may be used to attribute the special behavior of the variations in  $A$  values in the negative region to the intrinsic transition in the intermolecular forces and, accordingly, to the threshold state for the two types of singlet and triplet interactions. Although the LIR shows some deviations from linearity at high temperatures (see Table II), the deviations being consistent, one may still draw a reliable conclusion about the physical role of intercept,  $A$ , as done above.

For practical purposes, the Boyle temperature and the volume have been adopted in the application of the ISM equation of state [11]. The Boyle temperature and the volume of alkali metals have been determined in this work from a correlation in which the second virial coefficient is expressed as a polynomial in  $\Delta H_v$ , the heat of vaporization. The density at the freezing temperature plus the  $\Delta H_v$  are the scaling constants (in the correlation) for the calculation of  $\alpha$  and  $b$  in Eq. (4). The alkali metals, with particular properties mentioned previously, are not expected to follow the same correlation as a normal fluid, and therefore, such a procedure produced only the so-called quasi-second virial coefficient [26]. However, it has been shown that the quasi-second virial coefficients represent the physical properties in a real sense [26]. Thus, the above conclusion concerning the  $A$  values compared to the  $B_2$  values may be treated in a real sense.

With regard to the  $R^2$  values for dense normal fluids, LIR is found to be valid for temperatures up to twice  $T_B$ , well above the critical temperature  $T_c$  [1]. For the molten alkali metals, however (see Tables I and II), this work reveals that LIR is valid up to the critical temperature, which may be attributed to the intrinsic changes in the nature of intermolecular forces as the critical temperature is approached.

Two more points require explanation: first, the lack of experimental data does not allow us to determine the range of linearity of the LIR version of the ISM equation of state; and second, as the isotherms approach the critical temperature the deviations of the  $R^2$  values from unity gets larger, indicating that LIR might become nonanalytic at the critical point.

## 6. CONCLUSIONS

We have shown that  $(Z - 1)v^2$  varies linearly with  $\rho^2$  for molten alkali metals. The slope and the intercept of the present regularity are linear in  $1/T$ ; the regularities are consistent with the ISM equation of state, which is shown to be accurate for compressed fluids over a wide range of temperatures and pressures. We now have a new useful way of plotting data on the isotherms of liquid alkali metals. Moreover, the temperature dependences of the linear isotherm parameters for the alkalis are known. Also, we have found that  $A$  is an important parameter that may be used to assess the range of effective intrinsic intermolecular forces in molten alkali metals.

## ACKNOWLEDGMENTS

M. H. Mousazadeh is indebted to the authorities of the Razi University of Kermanshah for granting him a leave of absence. The support of this work by the Shiraz University Research Council is gratefully acknowledged.

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