J. Chem. Eng. Data **2010,** *55,* 1093–1099

Internal Pressures of Lithium and Cesium Fluids at Different Temperatures

Vahid Moeini*

Payame Noor University, Behshahr Center, Behshahr, Iran

In this paper, we use internal pressure to predict metal−nonmetal transitions in alkali metals. Isotherms of the internal pressure of cesium fluid versus molar volume show a maximum point around 1.3 $g \cdot cm^{-3}$ in agreement with X-ray diffraction and small-angle X-ray scattering. It is shown that at molar volumes higher than the maximum point the attractive force has a strong influence on the determination of internal pressure that similar studies have been made for negative compressibility. An accurate empirical potential was found for dense alkali fluids and used to test the applicability of the theory. These theoretical predictions are in good agreement with experimental results. Problems have led us to try to establish a function for the accurate calculation of the internal pressure and the prediction of metal−nonmetal transition alkali metals based on the internal pressure.

Introduction

Metallic fluids are generally considered to be monatomic simple liquids. They are an interesting and important class of liquids. Metallic fluids, and in particular those of the alkali metals, are of great interest in many space and nuclear power programs where coolants and working fluids are required at high temperatures. Thermophysical properties of saturated and superheated phases are needed for the design and development of these power systems.[1,2] The anticipated use of alkali metals of working fluids, heat transfer media, and lubricants in high-temperature energy-conversion systems has spurred considerable research on the thermophysical properties similar to the surface tension of these fluids.[3,4] The main industrial use for lithium is in ceramics, glass, and aluminum production, but its use in electric batteries and as a heat carrier in atomic fusion reactors will increase the demand.[5]

X-ray diffraction and small-angle X-ray scattering of cesium fluids have been measured by reducing electron density down to the range where the compressibility of the interacting electron gas has been theoretically predicted to become negative. It suggests that an attractive interaction among like charges, ions in this case, is enhanced.[6−9] Despite the fact that the description of the metallic fluids at the molecular level is very complicated, they obey some relatively simple rules.[10] Among these we refer to a general regularity which has been reported for pure dense fluids, according to which $(Z - 1)V^2$ is linear with respect to ρ^2, and each isotherm can be taken as,

$$(Z - 1)V^2 = A + B\rho^2 \tag{1}$$

where $Z \equiv pV/RT$ is the compression factor, $\rho = 1/V$ is the molar density, and A and B are the temperature-dependent parameters as follows:

$$A = A'' - \frac{A'}{RT} \tag{2}$$

$$B = \frac{B'}{RT} \tag{3}$$

Here A' and B' are related to intermolecular attractive and repulsive forces, respectively, while A'' is related to the nonideal thermal pressure and RT has its usual meaning.[11,12] The regularity was originally suggested on the basis of a simple lattice-type model applied to a Lennard−Jones (12-6) fluid. This regularity holds for densities greater than the Boyle density and temperatures lower than twice that of the Boyle temperature. The linear isotherm regularity, LIR, can be used to predict metal−nonmetal transitions.[13,14]

Another work has derived an equation of state for liquid cesium based on a suggested potential function of Lennard−Jones (6-3) in accord with the characteristics of large attraction and soft repulsion at the asymptotes of the interaction potentials.[15,16] By considering the interaction of the nearest adjacent atoms in a dense fluid, the equation of state predicts that $(Z - 1)V^2$ is linear with respect to $1/\rho$ for each isotherm.

$$(Z - 1)V^2 = C + B(1/\rho) \tag{4}$$

where C and B are temperature-dependent parameters as follows:

$$C = C_2 + \frac{C_1}{RT} \tag{5}$$

$$B = -\frac{B_1}{RT} \tag{6}$$

In the present work, we use the internal pressure to predict experimental regularities in lithium and cesium metals. The cohesive forces, which are the resultant forces of attraction and forces of repulsion between liquid molecules, holding a liquid together create a pressure within the liquid which has been termed the internal pressure.[17] It plays a central role in the manipulation of the Fist Law and applies to any substance. The internal pressure plays a major role in thermodynamics because it is a measure of the variation of the internal energy of a substance as the volume it occupies is changed at constant temperature. For a perfect gas, the internal energy is independent of the volume at constant temperature. If attractions are dominant in a real fluid, the internal energy increases with volume because the molecules become further apart on average. If repulsion is dominant, the internal energy decreases as the fluid expands.[18] Internal pressure, a fundamental liquid property, is closely related to the different properties of liquids such as ultrasonic velocity, free volume, viscosity, surface tension,

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* Author to whom correspondence should be addressed. E-mail: v_moeini@yahoo.com.

10.1021/je900538q

solubility parameters, and latent heat of vaporization in the liquid phase. Considering the internal pressure by modeling the average configurational potential energy and then taking its derivative with respect to volume predicts that the isotherm $((\partial E/\partial V)_T/\rho RT)V^2$ is a linear function of ρ^2, where E is the internal energy and $(\partial E/\partial V)_T$ is the internal pressure. The final result is therefore of the form

$$\left(\frac{(\partial E/\partial V)_T}{\rho RT}\right)V^2 = A + B\rho^2 \tag{7}$$

where the intercept A and the slope B are related to attraction and repulsion, respectively, and both depend on temperature. In practice, it shows that

$$A = \frac{A_1}{RT} \tag{8}$$

$$B = B_2 - \frac{B_1}{RT} \tag{9}$$

Thus, the intercept A and the slope B are linear in $1/T$. These problems have led to attempts to establish a function for the accurate calculation of the internal pressure based on the speed of sound theory for different fluids.[19]

The purpose of this paper is to point out that this general regularity applies to alkali metals. The regularity can be used for predicting a metal−nonmetal transition in alkali metals. When the transition occurs, $((\partial E/\partial V)_T/\rho RT)V^2$ is nonlinear in ρ^2 for alkali metals that are similar to LIR behavior.

The other fact which has been investigated in this work is a new regularity that has been used for a range of metal−nonmetal transitions of alkali metals based on the internal pressures that are calculated by the Lennard−Jones (6-3) potential function and using experimental data.[15] Considering the internal pressure by modeling the average configurational potential energy and then taking the Lennard−Jones (6-3) potential function derivative with respect to volume predicts that the isotherm $((\partial E/\partial V)_T/\rho RT)V^2$ is a linear function of $1/\rho$ when the transition occurs in alkali metals. The predictions are in agreement with experimental observations; the intercept A and the slope B are related to attraction and repulsion, respectively, and both depend on temperature.

Finally, we have performed a structural study of the expanded fluid cesium based on internal pressure. The experimental results show that the internal pressure maximum occurs at around 1.3 $\text{g}\cdot\text{cm}^{-3}$ or 0.097 $\text{L}\cdot\text{mol}^{-1}$ similar to X-ray diffraction and small-angle X-ray scattering measurements.[9,15] These structural features suggest that clustering occurs in the metallic fluid.

Theory

In the present work, we begin with the exact thermodynamic relation

$$(\partial E/\partial V)_T = T(\partial p/\partial T)_\rho - p \tag{10}$$

in which $T(\partial p/\partial T)_\rho$ is usually called the thermal pressure and $(\partial E/\partial V)_T$ is called the internal pressure.[20,21]

In the present work, we assume that any kinetic energy contribution to the internal energy E will vanish on taking the derivative, since the temperature is held constant.[11] We approximate the average potential energy by summing the contribution from the nearest neighbors only, assuming single inverse powers for the effective repulsion and attraction, that is,

$$U = \frac{N}{2}z(\rho)\left(\frac{C_n}{\bar{r}^n} - \frac{C_m}{\bar{r}^m}\right) \tag{11}$$

where U is the total potential energy among N molecules, $z(\rho)$ is the average number of nearest neighbors, $\bar{r}$ is the average distance between nearest neighbors, and C_n and C_m are constants. For a repulsive−attractive (n,m) potential, adjustable parameters n and m represent exponents of repulsion and attraction interactions, respectively. It is well-known that $z(\rho)$ is proportional to ρ, as is the case for liquid argon, rubidium, and cesium, and taking$\upsilon \approx \bar{r}^3$, U can be written as

$$\frac{U}{N} = \frac{K_n}{\upsilon^{(n/3)+1}} - \frac{K_m}{\upsilon^{(m/3)+1}} \tag{12}$$

where K_n and K_m are constants. Carrying out the differentiation, we obtain the internal pressure for dense fluids.[11,19]

$$p_{\text{int}} = \left(\frac{\partial E}{\partial V}\right)_T \approx \left[\frac{\partial(U/N)}{\partial \upsilon}\right]_T = B_1\rho^{(m/3)+2} - A_1\rho^{(n/3)+2} \tag{13}$$

where A_1 and B_1 are constants. For a large number of atomic and molecular fluids, the Lennard−Jones (12-6) potential function accounts for the pairwise interaction approximation between the fluid molecules undergoing dispersive interaction as the major interaction.[11,15,19] The interest in the Lennard−Jones function is also due to its simple form, which facilitates simple integration and differentiation desired for derivation of an analytical form of statistical mechanics functions. Despite the progress in understanding the electronic properties of expanded alkali metals, essentially not very much is known on the strong statistical mechanics state dependence of their effective interatomic interaction, especially the change in these interactions as the metal−nonmetal transition is approached.[7] The recent neutron scattering experiments for cesium as a function of temperature and pressure, however, are directed to investigate the more detailed density dependence of the effective interaction potentials of expanded alkali metals.[15] This requires a theory that further relates the structure factor to the interaction potential. Results from the neutron scattering study as a function of pressure have shown a change in the position of the first peak of the pair correlation function, denoting a slight change in the mean interatomic distance.[8,9] The analysis of data in general has shown that at high densities an alkali metal atom interacts with a repulsive soft core at small interatomic distances and with a weak attraction at interatomic distances.[22] At larger atomic separation, the potential function oscillates and takes an $m = 0$ asymptotic form.[15] On the other hand, by the integral equation theory, the effective pair potential of liquid cesium for a wide range of densities has been derived from the experimental structure factors using the inverse method; the derived pair potential function at low temperatures oscillates at large interatomic distances, but as temperature is increased, the oscillations are damped out. Also, as the temperature is increased, the long-range interaction would be characterized by a greater attraction.[9] The repulsive side of this potential has been analyzed in terms of $n = 3$. For rubidium, the larger the size of the alkali atom indicates a softer electronic cloud. It is well-known that the interionic dipole−dipole interaction has the effect of softening the pair potential. Because the ionic polarizability of cesium is larger than other alkali metals, the softening is also expected to be larger for cesium than other for alkali metals.[15,22] The foregoing analysis of the experimental data indicates the fact that the range of liquid metal densities correspond to the interatomic distances mainly located around the potential minimum and likely are extended to larger atomic distances than the equilibrium interatomic distance. Therefore, to use the Lennard−Jones (6-3) potential function to predict the statistical mechanics properties of liquid lithium and cesium metals to sufficiently accurate results, we should take $m = 0$ and $n = 3$.

Combining the foregoing results, we find the internal pressure for dense fluids based on the Lennard−Jones (6-3) potential function.[19]

$$\left(\frac{\partial E}{\partial V}\right)_T = -A_1\rho^3 + B_1\rho^2 \tag{14}$$

If we divide both sides of eq 14 by ρ^3, we obtain

$$\left(\frac{(\partial E/\partial V)_T}{\rho^3}\right) = -A_1 + B_1\left(\frac{1}{\rho}\right) \tag{15}$$

and from this simple model, we predict that the isotherm $((\partial E/\partial V)_T/\rho RT)V^2$ is a linear function of $1/\rho$ and so predict the temperature dependence of its parameters. The final result is therefore of the form

$$\left(\frac{(\partial E/\partial V)_T}{\rho RT}\right)V^2 = A + B\left(\frac{1}{\rho}\right) \tag{16}$$

where the intercept A and the slope B are related to repulsion and attraction, respectively, and both depend on temperature. In practice, we show that $A = A_2 - A_1/RT$ and $B = B_2 - B_1/RT$. Thus, the intercept A and the slope B are linear in $1/T$.

Experimental Tests

Recent technological advances have yielded increased applications for the alkali metals. An accurate knowledge of the physical properties of these fluids has become vital in many of these applications.[23] Initially, we present here a simple method of the ideas and then use the thermal pressure coefficient directly in place of using an equation of state to analyze experimental pVT data.[24−27] The equation of state described in this paper is explicit in Helmholtz energy A with the two independent variables density ρ and T. At a given temperature, the pressure can be determined by the Helmholtz energy.[19]

$$p(T, \rho) = -\left(\frac{\partial A}{\partial V}\right)_T \tag{17}$$

Using the general expression of the relation to the reduced Helmholtz energy $\phi = A/(RT)$ and its derivatives then gives

$$\frac{p(\delta, \tau)}{\rho RT} = 1 + \delta\phi_\delta^{\mathrm{r}} \tag{18}$$

where $\delta = \rho/\rho_C$ is the reduced density and $\tau = T_C/T$ is the inverse reduced temperature. Both the density ρ and the temperature T are reduced with their critical values ρ_C and T_C, respectively. Since the Helmholtz energy as a function of density and temperature is one of the four fundamental forms of an equation of state, all of the thermodynamic properties of a pure substance can be obtained by combining derivatives of the reduced Helmholtz energy ϕ. Here ϕ_δ and $\phi_\delta{}^{\mathrm{r}}$ are defined as.

$$\phi_\delta = \left(\frac{\partial\phi}{\partial\delta}\right)_\tau \tag{19}$$

and

$$\phi_\delta^{\mathrm{r}} = \left(\frac{\partial\phi^{\mathrm{r}}}{\partial\delta}\right)_\tau \tag{20}$$

Then, finally, to derive the thermal pressure coefficient, we need only convert the $\mathrm{d}\tau$ to $\mathrm{d}T$.

$$\mathrm{d}\tau = -\frac{T_C}{T^2}\,\mathrm{d}T \tag{21}$$

The above procedure leads to the acquisition of the thermal pressure coefficient from the reduced Helmholtz energy for real fluids.

$$\left(\frac{\partial p}{\partial T}\right)_\delta = \rho R\left[(1 + \delta\phi_\delta^{\mathrm{r}}) - \delta\tau\left(\frac{\partial\phi_\delta^{\mathrm{r}}}{\partial\tau}\right)_\delta\right] \tag{22}$$

First, for an experimental test, a new regularity that has been used for a range of metal−nonmetal transitions of the alkali metals are calculated by the Lennard−Jones (6-3) potential function and by using experimental data.[28,29] In Figure 1, the isotherms are plotted for liquid Li in the range of (600 to 1800) K. The intercept A and the slope B are related to attraction and repulsion, respectively, and both depend on temperature. Thus, the intercept A and the slope B are linear in $1/T$ (see Figure 2a,b). For comparison, for the coefficient of determination (R^2), the isotherms of internal pressure of the Lennard−Jones (6-3) potential function are compared with the same isotherms of internal pressures that are calculated using the Lennard−Jones (9-6) potential function and the Lennard−Jones (12-6) potential function. This comparison has been shown in Figure 3 for the Li fluid. It shows that below 1600 K the application of the isotherms of internal pressure of the (6-3) potentials is equal to the application with the same isotherms of internal pressures that are calculated using the Lennard−Jones (9-6) potential function and the Lennard−Jones (12-6) potential function. Beyond 1600 K for both the Lennard−Jones (9-6) and (12-6) potential functions, significant deviations are observed in R^2. Much of this effort concerns the metal−nonmetal transition, which occurs in the liquid when heat causes expansion.[7]

In this paper, we applied Li liquid for our primary test of the linear parameters of the isotherms in eq 16 using experimental data. The linear parameters of the isotherms of internal pressure using the (6-3) Lennard−Jones potential function for liquid Li are also shown in Table 1. This test has also been repeated for liquid cesium in the range of (600 to 1600) K using the

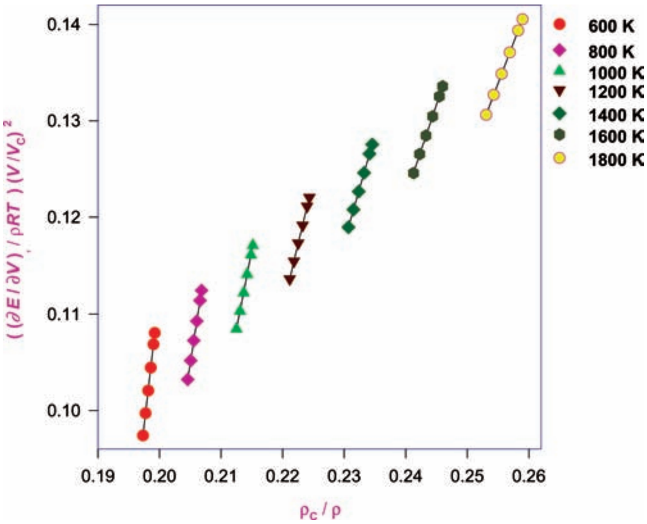

Figure 1. Validity of the linearity of the $((\partial E/\partial V)_T/\rho RT)V^2$ vs $(1/\rho)$ for different isotherms of Li in the range of (600 to 1800) K.

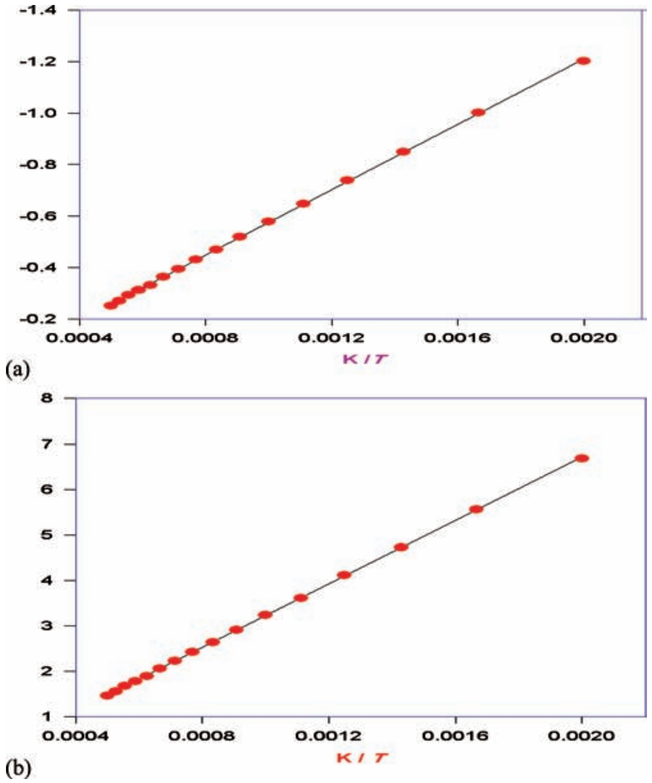

Figure 2. (a) Plot of *A* versus inverse temperature. Solid line is the linear fit to the *A* data points, for Li. (b) Plot of *B* versus inverse temperature. Solid line is the linear fit, for Li.

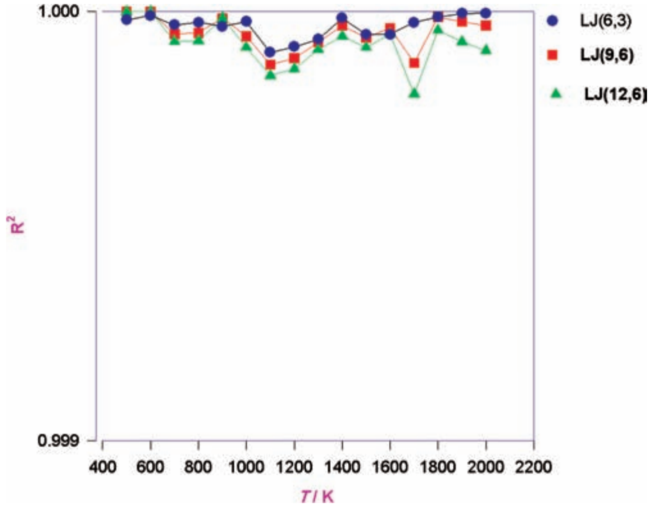

Figure 3. Coefficient of determination (R^2) for the same isotherms of internal pressure, calculated using the (6-3), (9-6), and (12-6) Lennard−Jones potential functions Li in the range of (600 to 2000) K.

Lennard−Jones (12-6) potential function. Linear parameters of the isotherms of internal pressure using the Lennard−Jones (12-6) potential function for liquid Cs are also shown in Table 2. While the transition occurs at 1350 K, a deviation from linearity predicted by internal pressure using the Lennard−Jones (12-6) potential function for a single-phase system is observed.[30,31]

In Figure 4, the isotherms of internal pressure of eq 16 are plotted for liquid cesium in the range of (600 to 1600) K; the intercept *A* and the slope *B* are related to attraction and repulsion, respectively, and both depend on temperature. The linear parameters of the isotherms of internal pressure using the Lennard−Jones (6-3) potential function for liquid Cs have been shown in Table 3. Isotherms of internal pressure are perfectly linear in the metal−nonmetal transition range. For comparison, for the coefficient of determination (R^2), the same isotherms of internal pressure calculated using the Lennard−Jones (9-6) and (12-6) potential functions are shown in Figure 5. Any potential function harder than the Lennard−Jones (6-3) potential function will deviate from the linear behavior more than the (6-3) isotherm of internal pressure over the whole liquid range. The isotherms of internal pressure of the Lennard−Jones (6-3)

Table 1. Reduced Intercept (*A*) and Slope (*B*), Coefficient of Determination (R^2), and Pressure Range (Δp) of the Data[a] for Li in the Equation $((\partial E/\partial V)_T/\rho RT)(v/v_C)^2 = A + B(\rho_C/\rho)$

T/K	*A*	*B*	R^2	Δp/MPa
500	−1.2019	6.6827	1	10 to 100
600	−1.002	5.5690	1	10 to 100
700	−0.8496	4.7294	1	10 to 100
800	−0.7393	4.1179	1	10 to 100
900	−0.6476	3.6146	1	10 to 100
1000	−0.5797	3.2384	1	10 to 100
1100	−0.5198	2.9108	0.9999	10 to 100
1200	−0.4704	2.6408	0.9999	10 to 100
1300	−0.4311	2.4237	0.9999	10 to 100
1400	−0.3950	2.2278	1	10 to 100
1500	−0.3646	2.0620	0.9999	10 to 100
1600	−0.3322	1.8935	0.9999	10 to 100
1700	−0.3133	1.7847	1	10 to 100
1800	−0.2936	1.6764	1	10 to 100
1900	−0.2712	1.5615	1	10 to 100
2000	−0.2532	1.4667	1	10 to 100

[a] Data from refs 28 and 29.

Table 2. Reduced Intercept (*A*) and Slope (*B*), Coefficient of Determination (R^2), and Pressure Range (Δp) of the Data[a] for Cs in the Equation $((\partial E/\partial V)_T/\rho RT)(v/v_C)^2 = A + B(\rho/\rho_C)^2$

T/K	*A*	*B*	R^2	Δp/MPa
500	0.8876	−0.0418	0.9999	10 to 100
600	0.7560	−0.0358	0.9998	10 to 100
700	0.6693	−0.0320	0.9997	10 to 100
800	0.6099	−0.0296	0.9995	10 to 100
900	0.5692	−0.0282	0.9991	10 to 100
1000	0.5412	−0.0276	0.9986	10 to 100
1100	0.5233	−0.0276	0.9979	10 to 100
1200	0.5129	−0.0281	0.9970	10 to 100
1300	0.5082	−0.0291	0.9960	10 to 100
1400	0.5074	−0.0305	0.9948	10 to 100
1500	0.5095	−0.0323	0.9939	10 to 100
1600	0.5133	−0.0344	0.9928	10 to 100

[a] Data from refs 28 and 29.

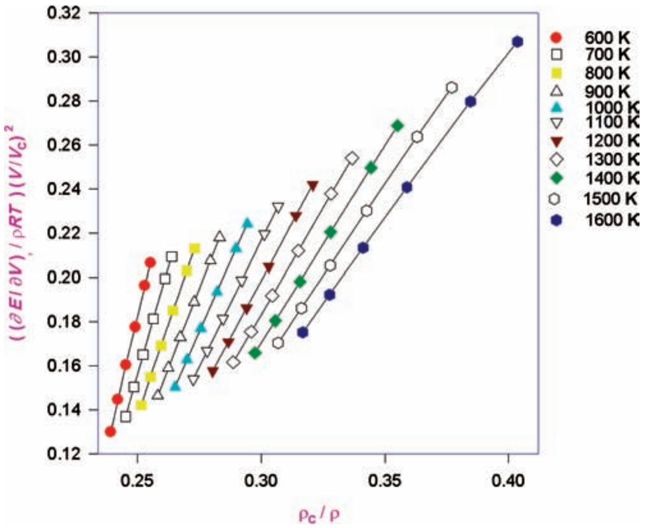

Figure 4. Plots of $((\partial E/\partial V)_T/\rho RT)V^2$ vs $(1/\rho)$ for Cs in the temperature range of (600 to 1600) K.

Table 3. Reduced Intercept (*A*) and Slope (*B*), the Coefficient of Determination (R^2), and the Pressure Range (Δp) of the Data[a] for Cs in the Equation ($((\partial E/\partial V)_T/\rho RT)(v/v_C)^2 = A + B(\rho_C/\rho)$)

T/K	*A*	*B*	R^2	Δp/MPa
500	−1.2627	5.9315	0.9999	10 to 100
600	−1.005	4.7477	0.9998	10 to 100
700	−0.8172	3.8938	0.9998	10 to 100
800	−0.6854	3.2921	0.9999	10 to 100
900	−0.5908	2.8570	0.9999	10 to 100
1000	−0.5203	2.5299	1	10 to 100
1100	−0.4679	2.2818	1	10 to 100
1200	−0.4274	2.0868	1	10 to 100
1300	−0.3947	1.9269	1	10 to 100
1400	−0.3655	1.7860	1	10 to 100
1500	−0.3369	1.6539	1	10 to 100
1600	−0.3059	1.5208	0.9998	10 to 100

[a] Data from refs 28 and 29.

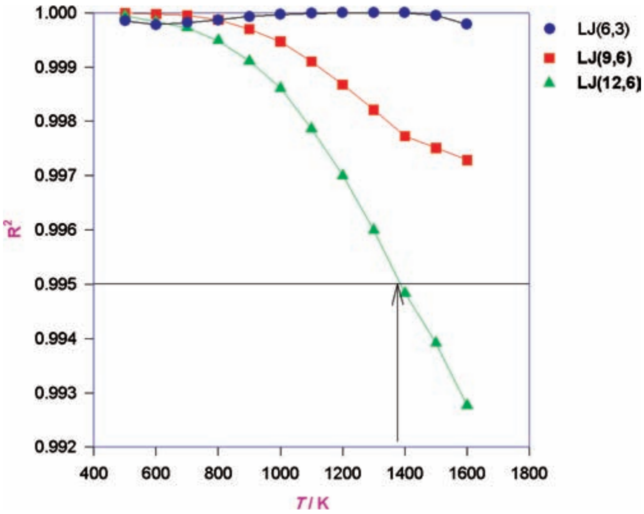

Figure 5. Coefficient of determination (R^2) for the same isotherms of internal pressure, calculated using the (6-3), (9-6), and (12-6) Lennard−Jones potential functions for Cs in the range of (600 to 2000) K.

potential function presented in this work apply quite well to liquid cesium over the whole liquid range including the metal−nonmetal transition, which onsets at a temperature of 1350 K. The linear limit of an isotherm of internal pressure is estimated by a limit of $R^2 \geq 0.995$.[15,19] A comparison of the coefficient of determination in Figure 5 reveals that the interaction potential in liquid cesium, both at low temperature and at high temperature, is modeled accurately by the Lennard−Jones (6-3) potential function. This makes the isotherms of internal pressure persist as being linear in both the metallic and the nonmetallic regions. The optical and the magnetic data suggest that the diatomic structure of cesium persists up to relatively high densities. This question is based on the view that the mechanism for the nonmetal−metal transition which occurs in diatomic molecules with increasing density may begin with the metallization of the diatomic system by an overlap of the valence and conduction bands, which at a higher density is followed by a gradual dissociation into a monatomic state. As noted above, liquid cesium at high densities shows characteristics typical of a nearly free electron metal. When the density is reduced below about 1.3 g·cm^{-3} or the temperature is increased up to 1350 K, quantitive changes develop. The measured electrical conductivity is clearly lower than the nearly free electron value. The failure of the nearly free electron theory reflects, most probably, cluster formation and the increased importance of soft potential.[7] Thus, a simple conclusion is that the harder the potential function is, the larger the deviations from linear behavior in the transition region are.

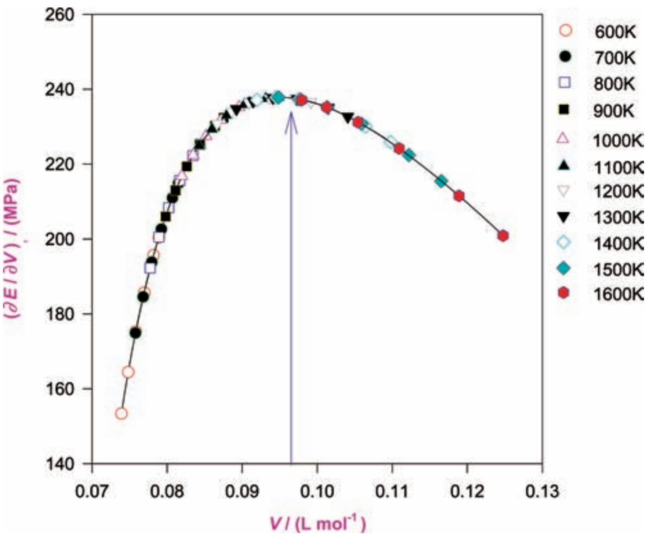

Figure 6. Internal pressures for an expanded volume of cesium fluid at various temperatures and pressures. Temperatures are indicated on the upper right-hand side of each data set.

Consideration of Internal Pressure in an Expanding Volume of Cesium Fluid

We have also calculated and plotted the internal pressure versus the molar volume at various temperatures (Figure 6). Isotherms of internal pressure of the cesium fluid versus molar volume show a maximum point at around 1.3 g·cm^{-3} or 0.097 L·mol^{-1}. In this paper, we also investigated the role of attractive and repulsive intermolecular energies on the behavior using internal pressure. We chose the Lennard−Jones intermolecular potential energy function because the Lennard−Jones potential function is also divided into attractive and repulsive parts.[32] It is well-capable of predicting the maximum point in the internal pressure−molar volume curve as well as the inflection point in the internal energy−molar volume curve. It is also shown that at molar volumes higher than the maximum volume the attractive forces have a strong influence on the determination of internal energy and internal pressure.[6,8,9]

By careful examination of the present results, it seems to us that this work contains a point of particular interest, a molar volume greater than the maximum, where internal pressure decreases as the molar volume increases at constant temperature. The physical interpretation in terms of molecular forces is as follows.

If the shape of the intermolecular potential function, $U(r)$, for molecules in fluids is considered, it is seen that $U(r)$ can be divided into two parts, attractive U_A and repulsive U_R parts, namely

$$U(r) = U_A + U_R \tag{23}$$

Differentiation at constant temperature with respect to volume gives:

$$(\partial U(r)/\partial V)_T = (\partial U_A/\partial V)_T + (\partial U_R/\partial V)_T \tag{24}$$

Namely,

$$P_i = P_{i,A} + P_{i,R} \tag{25}$$

where the attractive internal pressure, $P_{i,A}$, is seen to be positive, and the repulsive internal pressure, $P_{i,R}$, is negative. Figure 6 shows that, for the cesium fluid at a molar volume greater than the maximum, when the density is raised at constant temperature, the attractive pressure becomes predominant, and therefore the internal pressure increases.

Also, the authors reported an unusual behavior for the nearest-neighbor distance and coordination number for the cesium fluid of around 1.3 $g \cdot cm^{-3}$. The nearest-neighbor distance slightly decreases with decreasing density and stays almost constant until it reaches around 1.3 $g \cdot cm^{-3}$, but it starts to decrease with a further density decrease. The coordination number decreases substantially and almost linearly with decreasing density from (1.8 to 1.3) $g \cdot cm^{-3}$ and then shows a deviation from a linear dependence.[9] These structural features suggest that clustering occurs in the metallic fluid accompanying spatial atomic-density fluctuations.[7] While the transition is occurring, a number of changes similar to the coordination number in the liquid structure happen, and therefore a deviation from the linearity predicted by the LIR and of the isotherms of internal pressure of the Lennard−Jones (12-6) potential function for a single-phase system is observed.[8,9,13,14]

Results and Discussion

A general consistency was reported for pure dense fluids, namely, testing literature results for $p v T$ for pure dense fluids, according to which $(Z - 1)V^2$ is linear with respect to ρ^2 for each isotherm.[11] The regularity was originally suggested on the basis of a simple lattice-type model applied to a Lennard−Jones (12,6) fluid. The LIR has been used to predict the metal−nonmetal transition.[13] During the transition, a number of changes in the liquid structure occur, and therefore a deviation from the linearity predicted by the LIR for a single-phase system is observed.[33,34] The statistical mechanical theory of the mixture, along with the LIR, has been used to derive an appropriate equation of state for a mixture of metal and nonmetal, after the beginning of the transition.[13] On the basis of this objection, liquid alkali metals have been treated using statistical mechanics as an ensemble mixture of metal atoms and polyatom clusters. However, by this modeling, the deviations of isotherms from a linear behavior in the transition region have been attributed to the fractionation of the atomic liquid metal system into molecular clusters.[7,9,13,14]

In another work, it has been shown that a regularity, $((\partial E/\partial V)_T/\rho RT)V^2$, is a linear function of ρ^2 for each isotherm as both compressed liquids and dense supercritical fluids based on the Lennard−Jones (12-6) potential function.[19] This regularity is based on cell theory and considers only the nearest adjacent interaction.[11] In the present paper, using internal pressure regularity based on the Lennard−Jones (12-6) potential function for lithium and cesium metal liquids, experimental test data show that isotherms deviate from linear behavior as the transition temperature (about 1600 K for Li and 1350 K for Cs) is approached.[15] Therefore, we have shown in this work that using internal pressure based on the Lennard−Jones (12-6) potential similarly to the equation of state based on the Lennard−Jones (12-6) potential function predicts a metal−nonmetal transition in alkali metals.[13] The predictions are in agreement with experimental observations.

Another work explores further the idea that the cause of deviation of internal pressure using the Lennard−Jones (12-6) potential functions for each isotherm in expanded liquid alkali metals in the transition region is due to the underestimation of extra attractive potentials due to the development of polarized metal atoms in addition to polyatom clusters.[7,15] According to neutron scattering data and the application of an inversion method for interaction potential energy in liquid lithium and cesium, it presents a two-parameter pair type potential function. It is furnished to account suitably for the repulsion characteristics of alkali metals with soft electron clouds and the attraction characteristics of systems with appreciable Coulomb long-range attraction.[22,35,36] It has been shown that the larger the size of an alkali atom is, the softer the electronic cloud is. It is well-known that the interionic dipole−dipole interaction has the effect of softening the pair potential. From the foregoing analysis of the experimental data and from the fact that the range of liquid metal densities correspond to the interatomic distances mainly located around the potential minimum and internal pressure maximum, it is proposed that the Lennard−Jones (6-3) potential function would account for the interatomic interaction to model and thus to predict the internal pressure of liquid lithium and cesium significantly accurately. In this paper, we have also shown that the Lennard−Jones (6-3) potential function could account for the calculation of the internal pressures, particularly in the range that a liquid metal turns into the corresponding nonmetal.

Therefore, we have predicted in this work that internal pressure based on the Lennard−Jones (6-3) potential similar to an equation of state based on the Lennard−Jones (6-3) potential function remains linear over the entire liquid range including the metal−nonmetal transition range. The predictions are in agreement with experimental observations.

Conclusion

The unique properties of the liquid alkali metals and their vapors make them attractive as coolants and working fluids in heat pipes, turbines, and other heat transfer systems. These metallic fluids offer the capability of operating at high temperatures to take advantage of increased thermal efficiency. Design problems associated with new high temperature systems require an improved knowledge of the properties of the metals.[37] For extended space flight, turbine power convertors are being developed to supply power for auxiliary equipment. The turbines will require high-temperature working fluids, and the alkali metals with high heat-transfer coefficients and heats of vaporization are outstanding candidates.[38,39]

In the present work, the internal pressure of lithium and cesium for a wide range of temperatures are derived from density using the Helmholtz energy, which is based on using the (6-3) Lennard−Jones potential function and from the (12-6) Lennard−Jones potential function.[11,15,19] The results are discussed in comparison with those obtained previously for liquid cesium by equations of state. The density dependence of internal pressure derived for liquid cesium shows features in common with that for liquid lithium such that, with decreasing density, the repulsive part of the internal pressure becomes softer, and the resulting attractive part grows longer-ranged.[22]

In Figure 7, internal pressure that is derived from the Lennard−Jones (6-3) potential function is compared with internal pressure that is derived from Lennard−Jones (12-6) potential functions.[19] An appreciably softer repulsion and a greater attraction of the Lennard−Jones (6-3) potential function than the Lennard−Jones (12-6) potential function is noticeable. We believe that the characteristic attraction of the Lennard−Jones (6-3) potential function is mainly responsible for the persistent linear behavior of the isotherm internal pressure that is derived from in particular in the metal−nonmetal transition range.[15]

The other fact which has been investigated in this work is a new method for the prediction of metal−nonmetal transition alkali metals based on Lennard−Jones potential functions and using the internal pressure results. The internal pressure of an element is the main criteria for its metallic or nonmetallic

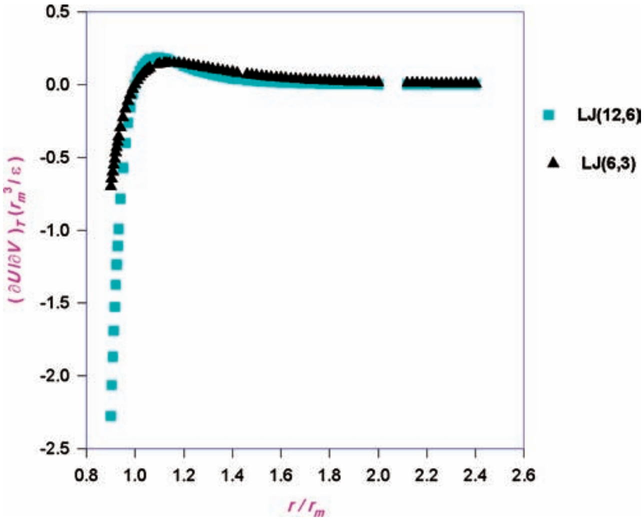

Figure 7. Reduced internal pressure calculated using (6-3) and (12-6) Lennard−Jones potential functions versus reduced interatomic separation. For long and short-range regions (where ε is the potential well-depth and r_m is the equilibrium interatomic distance).

character.[13,19] Such a conclusion is reasonable because for low temperatures (at high density) the electronic clouds significantly overlap the valence electrons and are expected to be delocalized and hence metallic characteristics are expected.[7] There is no definite way to distinguish the metallic and nonmetallic states, although some approximate approaches exist.[13] It is found that, when the transition occurs, a number of changes in the liquid structure happen. For example, the proportionality of density to the coordination number changes.[9]

Finally, we have performed a structural study of the expanded cesium fluid based on internal pressure. The experimental results showed that the maximum of the internal pressure is at around 1.3 $\text{g}\cdot\text{cm}^{-3}$ or 0.097 $\text{L}\cdot\text{mol}^{-1}$. Therefore, the structural features of the expanded fluid cesium such as local contraction and appearance of the internal pressure maximum in the metallic state at around 1.3 $\text{g}\cdot\text{cm}^{-3}$ or 0.097 $\text{L}\cdot\text{mol}^{-1}$ might be caused by the enhancement in the attractive interaction among the ions and interpreted as the emergence of such an inhomogeneous state induced by the negative sign of the dielectric function of the gas.

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Received for review June 26, 2009. Accepted January 7, 2010. We acknowledge the Payame Noor University for financial support.

JE900538Q