The Effective Potential Function of the Liquid Mercury on the Metallic and Nonmetallic States by Using the Experimental Internal Pressure

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Abstract

The major reason for the prediction of thermodynamic properties of mercury lies in the fact that its intermolecular interactions highly depend on temperature and density. Internal pressure is a good criterion to investigate the density dependence of the interatomic interactions. Because its physical base is a force tending to close together the molecules that is intermolecular interactions, and as well it can be calculated from the experimental *PVT* data. In this study the behavior of the experimentally calculated internal pressure of the mercury demonstrates three different metallic, M-NMT and nonmetallic regions. Then to investigate these different states the general form of the Lennard-Jones potential function [*LJ (m-n)*] has been chosen as the effective interaction potential and the experimentally calculated internal pressure has been used to estimate the values of *m* and *n* in each state.

Keywords: Liquid Mercury, Potential, Function, Internal Pressure, Metal Nonmetal Transition.

Introduction

Mercury has the lowest critical temperature of any fluid metals. Therefore, it has been investigated experimentally with accurate measurements in the critical region. These measurements involve its magnetic, electrical, structural, optical, and thermophysical properties with optimal control of temperature in the critical region.[1] The fundamental difficulty in dealing with fluid metals is that the electronic structures of liquid and gas phases are completely different. Experimental data clearly represent that mercury near its triple point (at densities larger than 11 g/cm3) follows the nearly free electron theory of metals that considers the nuclei completely shielded by delocalized electrons [2]. At lower densities (9-8 gcm^{-3}), the cohesion mechanism of its atoms will be suppressed by a partial localization of electrons and the

metallic character is changed to a nonmetal kind and a gradual metal-nonmetal transition (M-NMT) occurs.

The structure factors of the expanded liquid mercury for a wide density range has been studied using the effective pair potential obtained from pseudo-potential perturbation theory for liquid metal and by the Lennard-Jones potential for corresponding vapor. Although these pair potentials are valid in the two corresponding limiting cases, their validities are lost for those states that are near M-NMT [3,4]. From experimental data, it was concluded that the metal-nonmetal transition in liquid mercury is mainly due to lack of overlapping between the 6s and 6p bands [5,6,7]. Density dependence of mercury potential function has been subjected to the critical investigations [12] by using the experimental structure factor and theoretical modeling. Near the critical point, especially in the M-NMT region, there is no reliable theoretical method to derive an effective

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potential function for liquid metals accurately. Indeed, at high densities near the triple point the effective pair potential function, obtained from the nearly free electron model, can reproduce the thermodynamic properties quite well, though it gives less satisfactory results in the expanded liquid metals at low densities. Therefore, the accuracy of theoretical studies on the thermodynamic properties of liquid metals is subjected to the accuracy of pair potential function describing the intermolecular interaction of these metals. Recently a thermodynamic regularity has been derived for liquid mercury on the whole liquid range, by using a density dependent potential function and some simple thermodynamic arguments. The parameters of the obtained thermodynamic regularity have been used to calculate the molecular parameters of the potential function [8].

The physical base of the internal pressure is a force tending to close together the molecules that is intermolecular interactions [9]. On the other hand, the experimental *PVT* data can be used to calculate the internal pressure. Therefore, the experimental internal pressure is a good criterion for investigating the changes in the inter-atomic interactions.

Theory

Internal pressure is a partial derivative of the inner energy of a thermodynamic system with respect to volume multiplied by (-1):[9]

$$P_i = -\left(\frac{\partial U}{\partial V}\right)_T \qquad (1)$$

Internal pressure determines the tendency of intermolecular forces to resist against deformation of the volume of liquid in equilibrium process of isothermal expansion. In this study to derive a general formula for the internal pressure, the general form of the Lennard-Jones potential function [*LJ (m-n)*] Eq. (2) has been chosen as the effective interaction potential.

$$u(r) = A\varepsilon\left[\left(\frac{\sigma}{r}\right)^m - \left(\frac{\sigma}{r}\right)^n\right] \qquad (2)$$

where *A* is a constant, ε is the potential well depth, and σ is the molecular hard diameter. The potential function (2) obeys boundary conditions such that

$$r_m = \left(\frac{m}{n}\right)^{1/m-n}\sigma \qquad A = \left(\frac{m}{m-n}\right)\left(\frac{m}{n}\right)^{n/m-n}, \qquad (3)$$

To evaluate the interaction potential of atoms in liquid mercury the total pairwise additivity has been assumed. Then, the total potential energy U of a liquid system containing N atoms is calculated as

$$U(\mathbf{r}_1,...,\mathbf{r}_N) = \sum_{1\geq i>j}^{N} u(\mathbf{r}_i,\mathbf{r}_j) \qquad (4)$$

where pair potential $u(\mathbf{r}_i,\mathbf{r}_j)$ is often assumed to depend only upon the distance $\mathbf{r}_{ij} = |(\mathbf{r}_i - \mathbf{r}_j)|$ between the *i*th and *j*th pair of molecules located at positions r_i and r_j, respectively. Furthermore, we assume that all of the N atoms interact in pairs like a pair of atoms 1 and 2 with pair potential $u(\mathbf{r}_{12})$ and thus, we calculate the potential energy as

$$U(\mathbf{r}_1,...,\mathbf{r}_N) = \frac{N}{2}u(\mathbf{r}_{12}) \qquad (5)$$

where the factor $1/2$ is used to follow the restriction $i > j -$ excluding identical interatomic interaction potential energy.

To derive a general formula for the internal pressure the equation $v = K r^3$ has been used. K is a constant characteristic of the unit cell of mercury. Then the potential function Eq.(2) can be written as

$$\frac{U}{N} = \frac{A}{2}\varepsilon\left[\frac{\sigma^m}{K^m v^{\frac{m}{3}}} - \frac{\sigma^n}{K^n v^{\frac{n}{3}}}\right] \qquad (6)$$

By derivation of the potential function with respect to volume, the following relation has been obtained for the internal pressure in the metallic region (densities larger than 11 g/cm^3),

$$P_{\text{int}} = \frac{F_m}{v^s} - \frac{G_m}{v^q} \qquad (7)$$

Where *s* and *q* are $m/3+1$ and $n/3+1$ respectively, and

$$F_m = \frac{A}{2}\varepsilon\left(\frac{\sigma}{K}\right)^m \frac{m}{3} \qquad G_m = \frac{A}{2}\varepsilon\left(\frac{\sigma}{K}\right)^n \frac{n}{3} \qquad (8)$$

Results and Discussion

The experimental PVT tabulations measured for mercury have been used [10]. The calculated internal pressure versus volume on the whole liquid range (densities from $13.85 gcm^{-3}$ to 7.05 gcm^{-3}) has been shown in Fig. 1. In this figure, a change in the behavior of the internal pressure has been observed two times, and hence clearly three different regions have been detected. These regions have been separated by dashed lines. The first one that has a regular treatment is the metallic region from the density 13.85 gcm^{-3} to 11.05 gcm^{-3}, and the third one is the non-metallic region is corresponded to the temperatures more than $1823 K$ and the densities less than 8.35 gcm^{-3}. The irregular transition region is between these two regular ones. From the experimental structure factor data, mercury metal-nonmetal transition state begins at 1273 K, 10.98 gcm^{-3} and finishes at 1803 K, 6.8 grcm^{-3} [10].
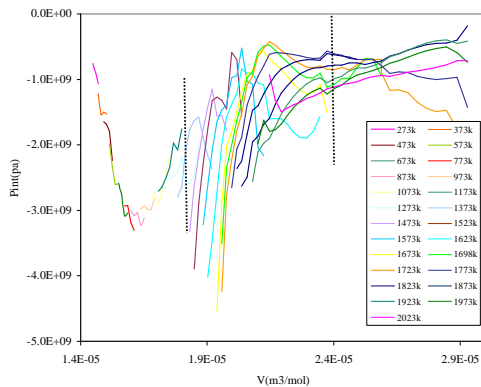

Fig. 1. The internal pressure versus volume on the whole liquid range, densities from 13.85 gcm^{-3} to 7.o5 gcm^{-3}.

As it has been shown in Fig. 1, P_{int} versus V in the metallic region can be adjusted in a second order polynomial. To estimate the parameters of Eq. (8), $v_\circ$ has been defined as the volume in $P_{int} = 0$ and v_1 is the volume corresponded to the minimum internal pressure.

$$v_\circ^{s-q} = \frac{F_m}{G_m} \qquad v_1^{s-q} = \frac{s}{q}\frac{F_m}{G_m}$$

$$\left(v_1 / v_\circ \right)^{s-q} = \frac{s}{q} \qquad\qquad (9)$$

If the parameters P and C have been defined as $s-q$ and $v_1 / v_\circ$ respectively. q can be written as $q = \frac{P}{C^P - 1}$. It is a function of P and C. Then Eq.(8) has been found the following form

$$P_{int} = \frac{F_m}{v^{P+q}} - \frac{G_m}{v^q} \qquad\qquad (10)$$

To determine the G_m, F_m, C and P, the experimental values of the internal pressure in each temperature can be fitted in this equation. Then m and n have been calculated from the obtained S and q.

In Fig. 2, the experimental internal pressure in the metallic region, its fitting in the Eq. (10) and the second order polynomial fitting have been shown. The obtained parameters are represented in Table 1. The values $m \cong 27$ and $n \cong 18$ have been calculated from s and q. This obtained hard potential function may be attributed to the hard repulsion of the closed shell $6s^2$ electronic structure and the using of the high pressure experimental data.
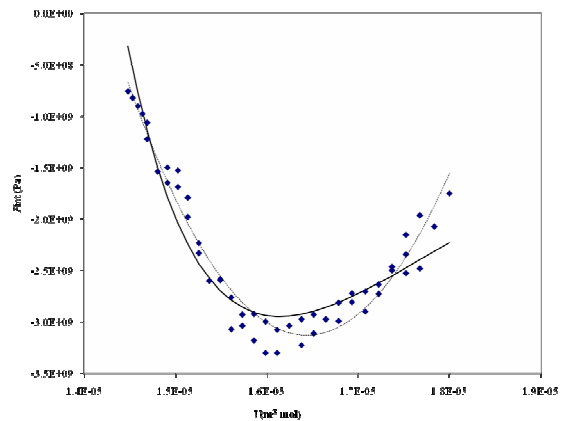

Fig. 2. The internal pressure versus volume in the metallic state densities from $13.85 gcm^{-3}$ to $11 gcm^{-3}$.

Table 1. The obtained parameters for the metallic state.

F_m	1.42E-40
G_m	2.87E-26
P	2.95
C	1.12
q	7.1
s	10.05

Bold line is fitting in Eq. (10) and dashed line is the second order polynomial fitting

In the non metallic region, as it can be observed in Fig. 3, a third order polynomial is suitable to fit the experimental internal pressure. Hence in addition to v_1 , v_2 is defined as the volume in which the second derivative is zero.

$$v_2^{s-q} = \frac{s(s+1)}{q(q+1)} \frac{F_{nm}}{G_{nm}}$$

$$\left(v_2/v_1\right)^{s-q} = s+1/q+1 \qquad (11)$$

If the parameters D has been defined as v_2/v_1 then it can be concluded that $q = \frac{P}{D^P - 1} - 1$ and then Eq.(8) has been written as

$$P_{int} = \frac{F_{nm}}{v^{P+q}} - \frac{G_{nm}}{v^q} \qquad (12)$$

Finally, from the experimental values of G_{nm}, F_{nm} , D and P , m and n have been obtained in the non metallic region.
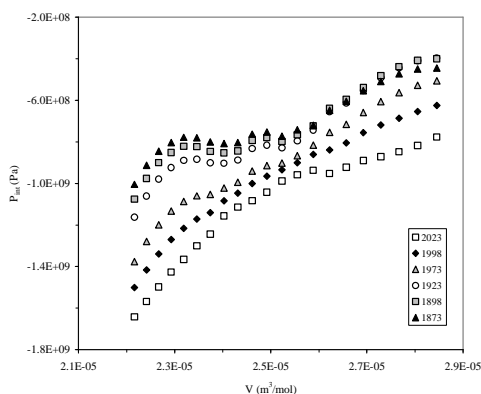

Fig. 3. The experimental internal pressure versus volume in the non metallic state densities between 9 gcm^{-3} and 7gcm^{-3} , the temperature from 1873K to 2023K .

The average value of the internal pressure in the non metallic region, the temperature from 1873K to 2023K and the densities between 9gcm^{-3} to 7gcm^{-3} are shown in Fig. 4. In this figure also the fitting of the experimental internal pressure in the Eq. (12) and the third order polynomial fitting have been shown. The obtained parameters are represented in Table 2, by this method. The values $m \cong 14$ and $n \cong 6.6$ have been calculated for the non metallic region. The effective potential function of the non metallic state has been reported similar to the Lennard-Jones (12-6) potential function [11].
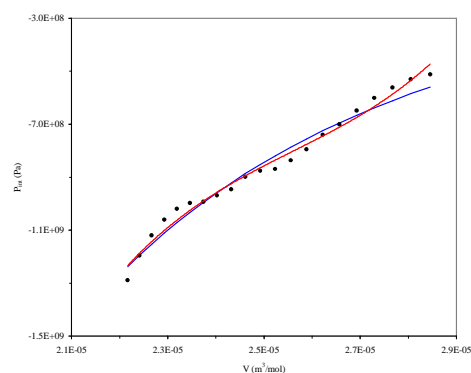

Fig. 4. The average internal pressure versus volume in the non metallic state. The blue line is its fitting in eq. (12), and the red line is the third order polynomial fitting.

Table 2. The obtained parameters for the non metallic state.

F_{nm}	3.65E-19
G_{nm}	7.97E-07
P	2.5
D	1.205
q	3.2
s	5.7

The metal non metal transition for mercury occurs in a wide temperature and density ranges. As it was observed in Fig. 5, in this region the calculated internal pressure from the experimental data is almost confused and have very irregular behavior. By the method of this work, it is not possible to report particular values for the m and n parameters of the potential function. But from a qualitative point of view, the behavior of the internal pressure in this region has two different features. In each temperature for densities near the metallic region its behavior is similar to this state and in the lower densities its

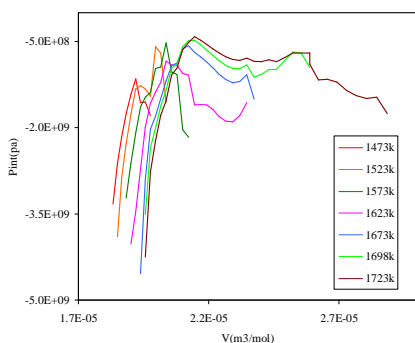changes is almost like to the non metallic state.

Fig. 5. The experimental internal pressure versus volume in the metal-non metal state.

Conclusion

The intermolecular interactions in liquid metals highly depend on temperature and density. This density dependence of the potential function has been subjected to the critical investigations by using the experimental structure factor and theoretical modeling. Internal pressure is a good criterion to investigate the density dependence of the interatomic interactions. Because its physical base is a force tending to close together the molecules that is intermolecular interactions, and as well it can be calculated from the experimental PVT data.

In this study the behavior of the experimentally calculated internal pressure of the mercury demonstrates three different metallic, M-NMT and nonmetallic regions. In the metallic region, the values $m \cong 27$ and $n \cong 18$ have been calculated as the powers of LJ (m-n) potential function. This obtained hard potential function maybe was attributed to the hard repulsion of the closed shell $6s^2$ electronic structure and the using of the high pressure experimental data. By this method, in non-metallic region the values $m \cong 14$ and

$n \cong 6.6$ have been calculated. It is in good agreement with the reported effective potential function of the non metallic state as LJ (12-6) potential function [10]. In the metal-non metal transition region the calculated internal pressure is almost very irregular. By the method of this work, it is not possible to report particular values for the m and n parameters of the potential function.

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