Computer Simulation and Modeling the Metal to Insulating Transition of liquid Mercury via Pair, Empirical and Many-Body Potentials

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Research Article

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Abstract

In this study Monte Carlo simulations were carried out to detect the metal insulator transition in liquid mercury by changing the static properties at microscopic scale. In the simulations pair, empirical, and many-body potentials governs metal–metal interactions in the canonical ensemble. The structural and thermodynamic changes over the wide of temperature range from 773 to 1773 K are described in the first coordination shell and residual internal energy, respectively. The results reveal that during the simulated heating process the properties undergo significantly change at 1673 K, which is in connection with the metal nonmetal transition in the liquid. These findings coincide with the experimental observations of this thermodynamic phenomenon. Notably, the free energy of association that renders the system to this thermodynamic state is estimated.

1. Introduction

Mercury metal (Hg) is unique elemental which is liquid at room temperature. In spite of controversy about its toxicity, toady mercury due to dissolves nearly all metals, is used in a variety of industrial application such mercury in medicine and industry i.e., dental amalgam [1], energy production [2], utilization mercury self-assembled monolayers (SAMs) as semiconductor device [2, 3], liquid Hg as a base for Langmuir films of imidazolium-based ionic liquids for electrochemical applications [4]. On other hand, the technology development of removal and capture of mercury as contamination is one of vital issue in environmental ecosystem in recent years, which has widely probed by both experiments and simulations studies [5, 6, 7, 8, 9]. Hence, for supplementary and help the above-mentioned aspects, further explores in properties, and structural phase transition of liquid Hg is worthily, particularly when the liquid change to liquid semiconductor or liquid insulator state.

Due to related technical difficulties in dealing with experimental measurement especially to the high temperatures, computer simulation currently is a powerful and convenient tool to study of the properties at microscopic level. It can remedy of experimental information.

In this simulation study, focus on the metal to nonmetal transition of the expanded liquid Hg in the framework of thermodynamic and structural properties. Hence, the wide of temperature range from 773 K to 1773 K and corresponding experimental densities were preferred.

The metal nonmetal transition (M-NM) that is fascinating phenomenon is observed firstly in 1940 for fluid mercury [10, 11]. Since then, researchers have aimed constantly for detecting of this phenomenon in both theoretical and experimental approaches. Briefly, the determination of the transition which was probed within a change in special properties based on different methodologies, are as following:

Statics properties; structure factors, $S(Q)$, and pair correlation function, $g(r)$, obtained by classical MD [12] or *ab initio* MD [13, 14], Reverse Monte Carlo (RMC) on X-ray diffraction of $S(Q)$ [15], properties change through equations of state [16, 17, 18, 19], as well as dynamics properties; diffusion coefficient, shear viscosity by *ab initio* MD [14].

In the same way, experimental procedures such measurements of the sound velocity (SV) based on the techniques of pulsed phase-sensitive [11, 20], ultrafast acoustics (temporal) method [21], X-ray scattering (IXS) [22, 23], and calorimetric measurements of specific heat [24], were utilized for characterization this phenomenon.

Notably, the conclusion of all these deferent methods, theoretical or practical confirmed that the M-NM transition is occurred at density nearness 9 g/cm^3 . In the vicinity of this density the transition is appeared within the alteration of aforesaid properties.

In this study Monte Carlo (MC) simulations were conducted to study M-NM transition in liquid mercury. The changing in structure and thermodynamics properties specifically coordination number, and excess internal energy is used to acquire this transition.

Remarkably, probing on this phenomenon the through pair, empirical and many body potentials herein is for the first time.

2. Modeling And Simulation

Monte Carlo (MC) simulation was performed in the NVT ensemble to probe the phase transition of metal to nonmetal of liquid mercury. The MC method is based on the Metropolis algorithm [25], which the positions of the atoms are allowed to change between the old and new state [25, 26]. This procedure is continued until equilibration is achieved by convergence of the energy.

The cubic cell of side L corresponding to the experimental density ρ at the given temperature was chosen (See Table 1). The periodic boundary conditions were employed in all three directions. The pair potentials were truncated at the cut-off radius 3.5 times of atomic diameter. Of the 4×10^7 configurations generated in the simulation, the first half were propagated to reach equilibration and the rest were used for statistical analysis and ensemble average calculations.

The atomic interactions were modeled through Lennard-Jones (LJ), empirical and many-body potentials that are described concisely as following;

A: Lennard-Jones Potential Model

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where r is the distance between two interacting fluid atom, σ denotes the LJ atom–atom collision diameter, and ε is the LJ fluid–fluid potential well-depth, in which their values elsewhere [30].

B: Embedded Atom Model

The embedded atom model (EAM) is written as:

$$U = \sum_i \Phi(\rho_i) + \sum_{i>j} \phi(r_{ij}) \quad (2)$$

The first term is many-body interaction, which is embedding energy required for the placement of i -th atom in the electron cloud density (ρ_i) that is made by j neighbor atoms at the location of atom i . The second term is pair-wise contribution. The more details and a lot of potential parameters of the EAM are stated in reference [31, 32].

C: Empirical Potential Model

The form of the empirical potential is as following functional equation;

$$u(r) = A_0 \exp(-\alpha r) - A_1 \exp[-\beta(r - R_0)^2]$$

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The first term is Born-Mayer repulsion, while the latter is attractive part, in which A_1 is a parabolic function of the temperature (T) as:

$$A_1(T) = \sum a_i T^i$$

The potential parameters are given by Bretonnet et. al., [33].

3. Results And Discussion

In this study, the simulated statics properties namely configurational internal energy and the first coordination number of the liquid mercury at different thermodynamic states are utilized for examining the *M-NM* transition, that will be seen in the below sections.

3.1. Statics properties change

It should be noted that, EAM is a complicated potential function in which possess a lot of parameters in both pair and embedded parts. Therefore, initially to accuracy the program code that used here, the properties such excess internal energy (U_{exe}) at 773 K is reproduced in reference [31], which is -52.15335 kJ/mol, that is the same with the value of -52.16008 kJ/mol via MD method in this reference [31]. The U_{exe} from this reference is calculated by internal energy (U) i.e., $U_{\text{exe}} = U - 1.5 RT$, in which R is the universal gas constant. As well as, this reproduce scheme is used for the empirical potential (C), for instance the pair correlation function, $g(r)$, at 773 K is duplicated in reference [33] (supplied by Bomont), as shown in Fig. 2. As seen, the all $g(r)$ features namely the peaks position and their heights are exact matching in the comparison.

Then, the simulations are conducted and continued for the aim of this study for detecting how the thermodynamic phenomenon of metal nonmetal transition, affects on these properties at atomic level.

The structural change of liquid Hg, is depicted by the first coordination shell (Z) or liquid microstructure, that it estimated using integration on pair correlation function, $g(r)$, [34, 35] as;

$$Z = 2\rho \int_0^{r_p} g(r) 4\pi r^2 dr \quad (4)$$

Where r_p is the first peak position of $g(r)$ (3.05 Å) and ρ is the number of density.

The calculated Z values as function of temperature ($Z-T$), using pair, empirical and many-body potentials are illustrated in Fig. 1. Firstly, the overall feature of this curve coincides with previous studies [13, 15, 36, 37, 38], that manifest there is an inhomogeneous expansion. Because, the first peak position in $g(r)$ as nearest neighbor distance, based on three model potentials (A,B,C) mainly remains constant, while the trend of coordination number turns down.

The figure of $Z-T$ indicate that at 1673 K corresponding density of 9.25 g/cm³, the slope of curve or the rate of change in the decreasing of Z in two side of this temperature, is evidently different. The slope of curve for $T \leq 1673$ K (the range of 773–1673 K) slightly decreasing, while for $T \geq 1673$ K (the variety of 1673–1773 K) significantly decreases. The slopes of the curve along with these two temperature range, cross at 1673 K, as clear in the figure. Consequently, at 1673 K a distinctive change in microstructure of the liquid occurs, which is connected to metallic to nonmetallic (M-NM) phenomenon. Hence, this instability in the liquid microstructure is driving force for altering metal state into insulating ones. On the statistical mechanics language, as thermodynamic states change toward the nonmetallic phase, the local aggregated of Hg atoms (molecular-like) emerges in the system [13], accordingly, the phase transition (M-NM) arises. Therefore for observation of this issue, the average ensemble of neighboring distribution for each Hg atoms is calculated by having geometric locations of atoms in the simulation box (i.e., $x^2 + y^2 + z^2 \leq r_p$). The comparison of neighboring distribution in the metallic state and nonmetallic through EAM is plotted in Fig. 3, a similar

curve was resulted for the others potential models (not shown). This plot characterizes a significant feature, that in nonmetallic state more fraction of atoms tendency to adapt one neighboring (dimer-like) distribution. Also, the existence of the dimer-like of Hg is experimentally detected [39], and coincides with the neighboring distribution feature in this study. In metallic bond language, emergence of these dimer-like species lead to localized conduction electrons in the system and hence insulating or semiconductor state consequences. This issue coincides with the value of free energy association (ΔA_{ass}) between atoms in the system for metallic and nonmetallic state that estimated through pair, many body and empirical potentials, as listed Table. 2. The ΔA_{ass} is estimated via following formula [40, 41]:

$$\frac{\Delta A_{ass}}{k_B T} = -\ln \left[\frac{4\pi}{V} \int_0^{r_p} \exp\left(-\frac{w(r)}{k_B T}\right) r^2 dr \right] \quad (5)$$

Where $w(r)$ is potential of mean force and V is a normalization factor for correlation length and volume of the first coordination shell.

As witnessed from the value of ΔA_{ass} in table. 2, the nonmetallic state (1673 K) exposes more positive free energy of association with respect to metallic (773 K) ones, that point out the association among atoms in the entire system is declined. As the snapshots (See Fig. 4) show, in the nonmetallic state the space among atoms is significantly increased with respect to metallic state. Hence, the lack of sufficient packing of atoms or the absence of effective spatial distances between atoms in system is resulted in the nonmetallic phase.

Additionally, the excess internal energy as function of temperature ($U_{ex} - T$) is visualized in Fig. 5. As can be seen, there is a particular feature in $U_{ex} - T$ curve, in which it exposes upward curvature as thermodynamic state approaching the nonmetallic phase (1673 K). The boundary of changing trends is visualized by vertical dashed line in this figure. Furthermore, in this figure, a comparison of the results within EAM is made with the evaluable data of MD based on EAM [31].

Moreover, it is not detected yet as the metal to nonmetal phase evolutions, how the excess internal energy alters. It should be noted that, in this figure the significant change in excess energy that is resulted from empirical potential (C) in the temperature range of 773–1473 K is not correlated to the phase transition. This characteristic relate to temperature dependency of parameter A_1 (see Eq. 3) in this potential equation. The empirical potential (C) in nonmetallic domain (1673–1773 K), point out the same trend with others potential models (A, B). Therefore, three model potentials in spite of their different numerical values due to their natures, forecast the nonmetallic range with the same trend. .

In short, the MC simulation of this study suggests metal to insulating transition occurs in 9.25 g/cm³. This result is in good agreement with both theoretically and experimentally studies [14, 21, 22, 37] that the transition is predicted around density of 9 g/cm³.

4. Conclusions

Metallic to insulating transition of liquid mercury is investigated in canonical ensemble by Monte Carlo simulation in the context of pair, empirical and many body interaction potentials.

The temperature dependencies of static properties are utilized to acquire the metal to nonmetallic transformation. The simulation results indicate that the first coordination number and configurational internal energy, differ markedly their trend and features, in the temperature of 1673 K (density of 9.25 g/cm³). Therefore in this thermodynamic state, a phase transition from metallic state to insulating ones occurs, which is consistent with experimental studies.

Especially, the simulated neighboring distribution estimates the more fraction of atoms tendency to form a dimer-like species in nonmetallic state.

Declarations

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Contributions

Hedayat Karimi: Conceptualization, methodology, investigation, writing the manuscript.

Availability of data and materials Not applicable.

Code availability Not applicable.

Conflict of interest The author declare no competing interests.

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Tables

Table.1 The cubic MC simulation cell of side L corresponding to the density ρ at the given temperature [27-29].

T/K	773	1073	1273	1473	1573	1623	1673	1723	1773
$\rho/(g/cm^3)$	12.40	11.57	10.98	10.26	9.81	9.53	9.25	8.78	8.26
$L/\text{\AA}$	23.7703	24.3256	24.7538	25.3198	25.7011	25.9504	26.2097	26.6692	27.2175

Table. 2. Free energy of association ($\Delta A_{\text{ass}}/k_B T$) between atoms in the system estimated within pair (A), many body (B) and empirical (C) potentials for metallic (M) and nonmetallic (NM) state.

state	A	B	C
NM (1673 K)	0.56226	0.54243	0.63603
M (773 K)	0.31461	0.39884	0.37599

Figures

Figure 1

Coordination number as function of temperature for expanded liquid Hg.

Figure 2

Comparison of $g(r)$ for liquid Hg at 773 K present simulation study with Bomont data [33].

Figure 3

Comparison of distribution of the fraction of atoms as a function of the number of neighbors in the first coordination shell for metallic (773 K) and nonmetallic (1673 K) states. Curves are trend lines.

Figure 4

Snapshot of metallic state (773 K) up panel, and nonmetallic state (1673 K) down panel.

Figure 5

Excess internal energy as function of temperature and the comparison of MD simulation within EAM potential [31]. The dashed vertical line indicates the boundary changing trends.

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