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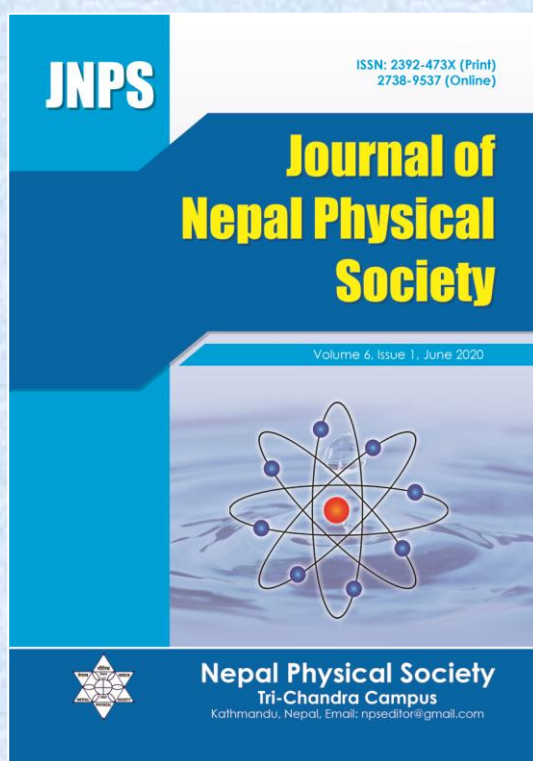
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## Static and Dynamic Properties of Elemental Liquid Pd: An Orbital Free Molecular Dynamic Study

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### Abstract

We have studied the static and dynamic properties of liquid metal, namely Pd at thermodynamic state  $T=1853\text{K}$  within the scope of the orbital free *ab-initio* molecular dynamics (OF-AIMD) simulation technique. In this simulation process, electronic energy is calculated by using the Hohenberg-Kohn version of DFT. Here the electron-ion interaction energy functional is approximated by a local pseudopotential prescribed by Bhuiyan *et al.* The local density approximation is used to describe the exchange-correlation energy functional. The static structure factor,  $S(q)$ , pair distribution function,  $g(r)$ , coordination number,  $N_c$ , and isothermal compressibility,  $\kappa_T$ , are studied which are familiar as static properties. The single particle and collective dynamics namely diffusion coefficient, dynamic structure factor, velocity of sound, shear viscosity etc. are also studied. The results of calculation agree well with experimental as well as other theoretical values.

**Keywords:** DFT, Local Pseudopotential, LDA, OF-AIMD, Static and Dynamic properties.

### 1. INTRODUCTION

The orbital free *ab-initio* molecular dynamics simulation (OF-AIMD) technique is widely used in the study of physical properties of metallic systems in the liquid state. The OF-AIMD calculation is based on the density functional theory (DFT) [1, 2]. Using the DFT the ground state electronic energy of a collection of atoms for given nuclear positions as well as the forces on them, via the Hellmann-Feynman (HF) theorem are computed. Therefore, it is feasible to carry out MD simulation in which the ionic positions evolve like classical mechanics while the electronic subsystem evolves quantum mechanically (for details see ref. 3 and 4). From the point of view of scientific and technological interests Pd is an important transition metal that lies in the group of VIIIA in the periodic table. In the solid phase it has face centered cubic (*fcc*) structure, the density of it is  $10.5 \text{ gm/cm}^3$  and melts at  $1827.15 \text{ K}$  [5]. The ionic number density of liquid Pd, used in this work, is  $0.0594 \text{ \AA}^{-3}$  at  $T=1853\text{K}$ . Palladium is widely used in hydrogen purifying devices and medicine. It is also used for fabricating conducting nanowires in order to use in

electronics industry. Çoruh [5] studied some properties of liquid Pd at  $T=1853\text{K}$  using MD simulations with Sutton-Chen potential and Quantum Sutton-Chen potential. Alemany *et al.* [6, 7] also studied the quantities related to the atomic transport properties namely diffusion coefficient and shear viscosity of liquid Pd at temperature  $T=1853\text{K}$  using the Voter and Chen version of the embedded atom model (VC-EAM) potential. Bhuiyan *et al.* [8] studied the static and thermodynamic properties of liquid Pd using embedded atom method. Kart *et al.* [9] studied liquid properties of Pd-Ni metal alloys by employing the MD simulation with the use of quantum Sutton-Chen potential (Q-SC) model. Recently, González *et al.* [10] performed a KS-AIMD simulation study using Kohn and Sham density functional theory (KS-DFT) for liquid Pd near the melting point.

In the present OF-AIMD study, the thermodynamic state is specified by temperature  $T=1853\text{K}$ . The reason of considering this specific temperature of  $1853\text{K}$  is three-fold. First, the experimental data for static structure factor in both momentum and real

space are available for liquid Pd, which enabled us to fix parameters of the pseudopotential describing the external energy functional. Second, at this temperature other classical MD [5-7, 9, 11] and AIMD [10] results for some atomic transport properties are available in the literature, which have been useful to compare our results with. Third, this temperature is near the melting point of Pd, of course in the liquid state, which ensure that no order-disorder transition can happen in the sample. In this article we have studied some static and dynamic properties of liquid Pd near its melting temperature by employing the OF-AIMD method of simulation. AIMD approach [10] along with Kohn-Sham (KS) orbital is, in principle, very accurate, there is no doubt. But, in practice, there are some limitations of it [12]. The calculation of KS-orbitals in a condensed state is very expensive computationally, this eventually restricts the size of the sample only within one or two hundred of particles. On the other hand, the OF-AIMD method can ease this restriction on size and, can handle large sample size with a few thousand particles. Note that the larger the sample one can better mimic the real system, and to represent the real system is always a target of all kind of simulation methods. The main difference between the AIMD and the OF-AIMD is in the calculation of kinetic energy of electrons; in the latter it is done approximately. As good approximation methods to evaluate electronic kinetic energy [12] is available, it is found in the literature that the OF-AIMD sometimes describes dynamic properties better than the AIMD [10, 12-14]. In the present study for Pd we have experienced a similar trend. For example, OF-AIMD diffusion coefficient agrees better with value derived from the experimental viscosity by using the Stokes-Einstein relation (see below) than the AIMD value of Gonzalez *et al.* [10]. As the OF-AIMD method can convincingly include the size effects in the results of the dynamic properties of liquid metals, the present work with large sample is worthy. Pd is a transition metal lying in the *4d* series. So, *sd*-hybridization effect due to mixing of *sp* and *d* states is always there. Application of KS-AIMD to Pd will require to calculate much more orbitals than any non-transition metals. This obviously imposes further constraints on sample size. To avoid this situation application of the OF-AIMD is one of the best options. In the OF-AIMD we considered 500 ions in a periodic cubical box of size  $L=20.3420407\text{\AA}$ , that is consistent with the experimental ionic number density of the system. Exchange-correlation functional in the DFT is

treated with local density approximation (LDA). Here, the external energy functional in DFT is generally calculated by using the pseudopotential. In the present calculation we have used the pseudopotential developed by Bhuiyan *et al.* [15]. In order to account for the *sp-d* hybridization effects in the calculation of external energy functional, we follow the spirit of Moriarty's findings [16-18] like many other authors [19, 20] and, used a non-integral effective value for the chemical valence  $Z$ .

The outline of this paper is as follows. In section II we have briefly described the theories that are used in the present OF-AIMD simulation, giving some technical details, as well as the pseudo-potential describing the electron-ion interaction. In section III we have presented and discussed the obtained OF-AIMD results and compared them with available experimental data and other theoretical results. Finally, we have drawn a brief conclusion in the section IV.

## 2. THEORY

A simple liquid metal is considered as a disordered array consisting of  $N$  bare ions with valence  $Z$ , enclosed in a volume  $V$ , and interacting with  $N_e=NZ$  valence electrons over an electron-ion pseudopotential potential,  $v(r)$  [3, 21]. Applying the Born-Oppenheimer approximation, the total potential energy of the system can be stated as the direct ion-ion coulombic interaction energy plus the ground state energy of the electronic system belonging to the external potential formed by the ions,  $V_{\text{ext}}(\vec{r}, \{\vec{R}_l\}) = \sum_{i=1}^N v(|\vec{r} - \vec{R}_i|)$ ,

$$E(\{\vec{R}_l\}) = \sum_{i<j} \frac{Z^2}{|\vec{R}_i - \vec{R}_j|} + E_g[n_g(\vec{r}), V_{\text{ext}}(\vec{r}, \{\vec{R}_l\})] \dots\dots\dots (1)$$

where,  $n_g(\vec{r})$  and  $\vec{R}_l$  are the ground state valence electron density and the ionic positions, respectively. Using DFT, the ground state valence electron density,  $n_g(\vec{r})$ , can be found by minimizing the energy functional,  $E[n]$  defined by

$$E[n(\vec{r})] = T_s[n] + E_H[n] + E_{\text{xc}}[n] + E_{\text{ext}}[n] \dots (2)$$

Where the terms represent, respectively, the electronic kinetic energy,  $T_s[n]$  of a non-interacting system having density  $n(\vec{r})$ , the classical electrostatic energy (Hartree term),  $E_H[n]$ , the

exchange-correlation energy,  $E_{xc}[n]$ , for which we used the local density approximation and finally the electron-ion interaction energy,  $E_{ext}[n]$ , where the electron-ion potential is characterized by a local ionic pseudopotential,

$$E_{ext}[n] = \int d\vec{r} n(\vec{r})V_{ext}(\vec{r}) \dots\dots\dots(3)$$

We used an explicit, albeit approximate functional of the valence electron density for  $T_s[n]$ . Several expressions were proposed and in the present calculations we used an average density model [3, 17] given by  $T_s[n] = T_W[n] + T_\alpha[n]$ , where

$$T_W[n(\vec{r})] = \frac{1}{8} \int d\vec{r} |\nabla n(\vec{r})|^2 / n(\vec{r}) \dots\dots\dots(4)$$

is the well-known von Weizsäcker term, and

$$T_\alpha[n] = \frac{3}{10} \int d\vec{r} [n(\vec{r})]^{5/3-2\alpha} [\tilde{k}(\vec{r})]^2, \dots\dots\dots(5)$$

$$\tilde{k}(\vec{r}) = (2k_F^\circ)^3 \int d\vec{s} k(\vec{s}) w_\alpha(2k_F^\circ |\vec{r} - \vec{s}|), \dots\dots\dots(6)$$

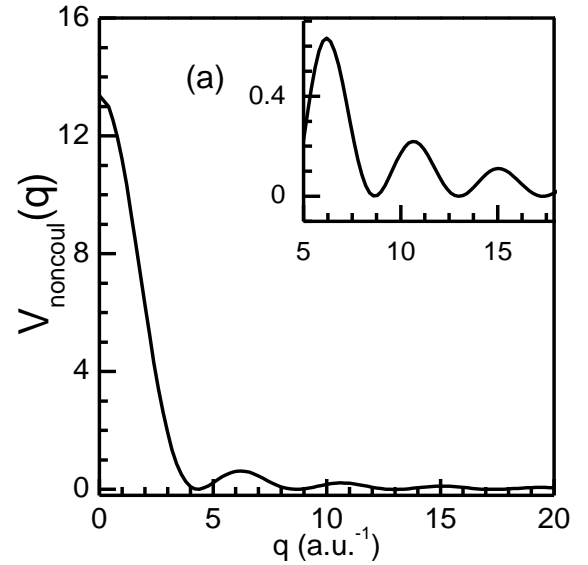
where  $k(\vec{r}) = (3\pi^2)^{1/3} [n(\vec{r})]^\alpha$ ,  $k_F^\circ$  is the Fermi wave vector for a mean electron density  $n_e = \frac{N_e}{V}$ , and  $w_\alpha(x)$  is a weight function picked in such a way that both the linear response theory (LRT) and Thomas-Fermi limits are properly recovered. Further details are given in reference [3, 21].

## 2.1 Pseudopotential

In the present study we have used a local ionic pseudopotential that describes the ion-electron interaction. Non-local pseudopotentials [22] constructed by fitting to some properties of the free atom [21, 23, 24] are employed in the AIMD simulations based on KS-DFT. However, in the present OF-AIMD approach, non-local pseudopotentials can not be used because the valence electron density is the basic variable. Therefore, the interaction among the valence electrons and the ions must be described by a local pseudopotential which is usually chosen to include an accurate description of the electronic structure in the physical state of interest. Bhuiyan *et al.* [15, 25] developed a local pseudopotential model which in conjunction with the OF-AIMD method has provided a good description of several static and dynamic properties of liquid metals near melting [4, 13-15]. The form of the local pseudopotential is

$$V_{ps}(r) = \begin{cases} F + E e^{-\frac{r}{f}} & \text{for } r < R_c \\ -\frac{Z}{r} & \text{for } r > R_c \end{cases} \dots\dots\dots(7)$$

where,  $F$  and  $E$  are constants,  $R_c$  is the core radius,  $Z$  is the effective number of nearly free  $sp$  - electrons and  $f$  denotes the softness parameter. Further details are given in reference [3, 4]. Fig. 1(a) shows the non-Coulombic electron-ion interaction in  $q$  space for liquid Pd at  $T=1853K$ .



**Fig. 1: (a)** Non-Coulombic part of the ionic pseudopotential for liquid Pd at  $T=1853K$ . The inset shows a magnified display of the oscillations.

## 3. RESULTS AND DISCUSSIONS

The OF-AIMD simulations have been performed for liquid Pd at thermodynamic state  $T=1853 K$ . In this simulation process, 500 particles were treated in a periodic cubic cell of size appropriate to the experimental ionic number density. Given the ionic positions at time  $t$ , the electronic energy functional is minimized with respect to  $n(\vec{r})$  represented by a single effective orbital,  $\psi(\vec{r})$ , defined as  $n(\vec{r}) = |\psi(\vec{r})|^2$  [3, 4]. The orbital,  $\psi(\vec{r})$ , is derived from the plane wave basis which is truncated at  $E_{cut} = 11$  Ryd for convenience. Using the quenching method, the energy minimizing with respect to the Fourier coefficients of the expansion is done at every ionic time step that yields the ground state electron density and energy. The Hellman-Feynman theorem is used for calculating the forces on the ions from the ground state energy. Newton's equations are solved by using the Verlet leapfrog

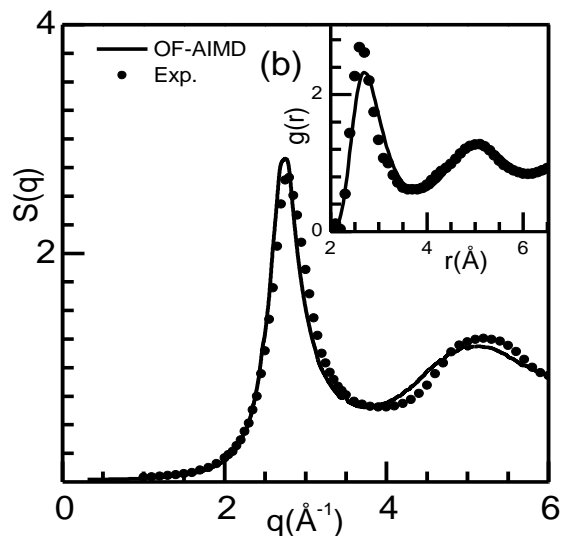
algorithm (with a time step of  $76 \times 10^{-4}$  ps) in order to update ionic positions and velocities with the progress of simulation. We have performed OF-AIMD calculation for 500 particles where equilibrium in the simulations lasted 38 ps. Static properties for instance structure factor, pair distribution function, coordination number, and isothermal compressibility are studied, where isothermal compressibility is obtained from the long wavelength limit of  $S(q)$ . Dynamical properties (both single particle and collective) such as dynamic structure factor, adiabatic sound velocity, diffusion coefficient, shear viscosity etc. are also computed. Unusually a good parameterization gives a minimum number of iteration steps. From the parameterization we have the pseudopotential parameters such as core radius  $R_c=1.45\text{au}$ , softness parameter  $f=0.30\text{au}$ ,  $sp$ -electron occupancy number  $Z=1.6$ , and constant  $F=0.005\text{au}$ . The Ewald radius is fixed at 5.00 au. For calculating the equilibrium properties, the system needed to be thermalized; indication of it was found when average energy, force and temperature remained unchanged during 5000 iterations. This implies that the system has been thermalized well and it is in the ground state.

### 3.1 Static Properties

In this section we have discussed the static properties like pair distribution function, coordination number, static structure factor and isothermal compressibility.

The simulated  $S(q)$  for l-Pd at  $T=1853\text{K}$  is shown in Fig. 1(b) together with the XR diffraction data [26]. Fig. 1(b) shows a reasonably good agreement with experiment, although the height of the main peak of our simulated  $S(q)$  is somewhat overestimated while the amplitude of the second peak is slightly underestimated. The main peak is located at  $q_p \approx 2.77 \text{ \AA}^{-1}$  whereas from the XRD data [26] it is observed at  $q_p \approx 2.76 \text{ \AA}^{-1}$ . Interestingly, our OF-AIMD results are better in agreement with experiment than that of KS-AIMD peak position ( $q_p \approx 2.79 \text{ \AA}^{-1}$ ) and height simulated by González *et al.* [10]. The isothermal compressibility  $\kappa_T$  is obtained from the relation  $S(0) = \rho K_B T \kappa_T$ , where  $K_B$  and  $T$  are Boltzman constant and temperature respectively [27]. A least square fit of  $S(q) = s_0 + s_2 q^2$  to the calculated  $S(q)$  for small  $q$ -values gives the value of  $S(0)$  and we obtained  $\kappa_T = 1.23 \pm 0.03$  (in units of  $10^{-12} \text{ cm}^2/\text{dyne}$ ). This is little bit larger than the experimental  $\kappa_T = 1.02 \pm 0.07$  (in units of  $10^{-12}$

$\text{cm}^2/\text{dyne}$ ) value [26]. González *et al.* [10] have reported,  $\kappa_T = 4.70 \pm 0.07$  (in units of  $10^{-12} \text{ cm}^2/\text{dyne}$ ) from their KS-AIMD study.



**Fig. 1: (b)** Static structure factor,  $S(q)$  and Pair distribution function,  $g(r)$  (inset) at  $T=1853\text{K}$  of liquid Pd.

The pair distribution function,  $g(r)$  for l-Pd at  $T=1853\text{K}$  is plotted in the inset of Fig. 1(b) along with the XR diffraction data [26]. Fig.1 (b) shows a good agreement with experiment [26], although the height of the main peak seems to be underestimated. We note here that the main peak of  $g(r)$  occurs at  $r_p \approx 2.70 \text{ \AA}$  and  $r_p \approx 2.60 \text{ \AA}$  for simulated and experimental [26]  $g(r)$ , respectively. While González *et al.* [10] have reported from their KS-AIMD study that the main peak of  $g(r)$  occurs at  $r_p \approx 2.69 \text{ \AA}$ . The concept of the coordination number, particularly the first coordination number  $n_1$ , is frequently used in the structural study of non-crystalline materials. The coordination number,  $N_c$  is calculated from the following relation [26],

$$N_c = \int_{r_0}^{r_m} 4\pi\rho r^2 g(r) dr \dots\dots\dots(8)$$

where,  $r_0 \approx 0$ ,  $r_m \approx 3.69 \text{ \AA}$  and  $\rho$  is the ionic number density. Our computed  $N_c \approx 11.65$ , which is closer to the experimental value,  $N_c \approx 10.90$  calculated from the experimental  $g(r)$  data [26]. A KS- AIMD study [10] gives  $N_c \approx 12.8$  having  $r_m \approx 3.77 \text{ \AA}$  of  $g(r)$ .

### 3.2 Dynamic Properties

In this section we have presented and discussed our results for the dynamic properties like self-diffusion

coefficient, self-intermediate scattering function, intermediate scattering function, dynamic structure factor, velocity of sound, transverse current time correlation function and shear viscosity.

### 3.3 Single Particle Dynamics

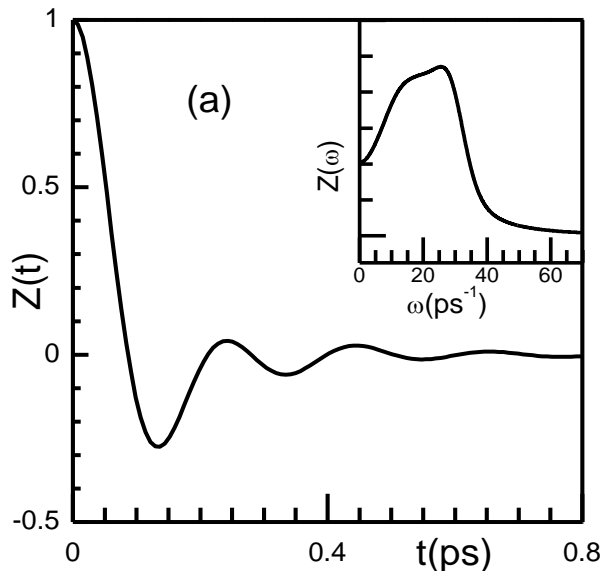
In present simulation, the self-diffusion coefficient can be easily obtained from the definition  $Z(t) = \langle \vec{u}(t) \cdot \vec{u}(0) \rangle / \langle u^2 \rangle$ , which stands for the normalized velocity autocorrelation function (VACF). The self-diffusion coefficient  $D$ , is calculated from the relation [27],

$$D = \frac{TK_B}{M} \int_0^\infty Z(t) dt \quad \dots\dots\dots(9)$$

where,  $K_B$ ,  $T$  and  $M$  are the Boltzman constant, temperature and mass of an atom respectively. We have also calculated the diffusion coefficient,  $D$  from the vicinity of mean square displacement  $\delta R^2(t) = \langle |\vec{R}(t) - \vec{R}(0)|^2 \rangle$  using the famous Einstein relation [27],

$$D = \lim_{t \rightarrow \infty} \frac{\delta R^2(t)}{6t} \quad \dots\dots\dots(10)$$

Both methods give the same result [28]. The calculated  $Z(t)$  for 1-Pd at  $T=1853K$  is plotted in Fig. 2(a),



**Fig. 2: (a)** Normalized velocity autocorrelation function,  $Z(t)$  of liquid Pd at  $T=1853K$ . The power spectrum of  $Z(t)$  is shown in the inset.

where we have observed the typical cage effect with a first minimum at  $t \approx 0.13ps$  and the subsequent oscillations seem to be weak. We recall that the negative values of  $Z(t)$  manifests backscattering due to cage effect [3, 4]. Following equations (9) and (10) we have calculated the self-diffusion coefficient and, obtained a value of  $D = 0.40 \pm 0.01 \text{ \AA}^2 ps^{-1}$ . The CMD study by Kart *et al.* [9] reports  $D=0.498 \pm 0.005 \text{ \AA}^2 ps^{-1}$  and  $D=0.494 \pm 0.007 \text{ \AA}^2 ps^{-1}$  from  $Z(t)$  and mean square displacement approaches, respectively. For comparison, we note here that the CMD study of Alemany *et al.* [7] using the TB-SMA method computed  $D=0.403 \pm 0.003 \text{ \AA}^2 ps^{-1}$ . In another CMD study using embedded atom model, Alemany *et al.* [6] have also calculated  $D=0.38 \pm 0.004 \text{ \AA}^2 ps^{-1}$ . We are not aware of any experimental data for  $D$  for liquid Pd at  $T=1853K$ . A MD simulation study [5] have reported  $D=0.5029 \text{ \AA}^2 ps^{-1}$ . Our result is very close the values found by Alemany *et al.* [6, 7]. The KS-AIMD calculation done by González *et al.* [10] yielded  $D_{KS-AIMD} = 0.27 \pm 0.02 \text{ \AA}^2 ps^{-1}$ . The MD study of J. Mei *et al.* [11] have reported  $D=0.449 \pm 0.007 \text{ \AA}^2 ps^{-1}$  for  $T=1818K$ , which is also agrees well to our present result. As we do not have any direct experimental data for diffusion coefficient,  $D$  we have alternately used Stokes-Einstein relation [29],

$$D = \frac{K_B T}{2\pi\eta r_p} \quad \dots\dots\dots(11)$$

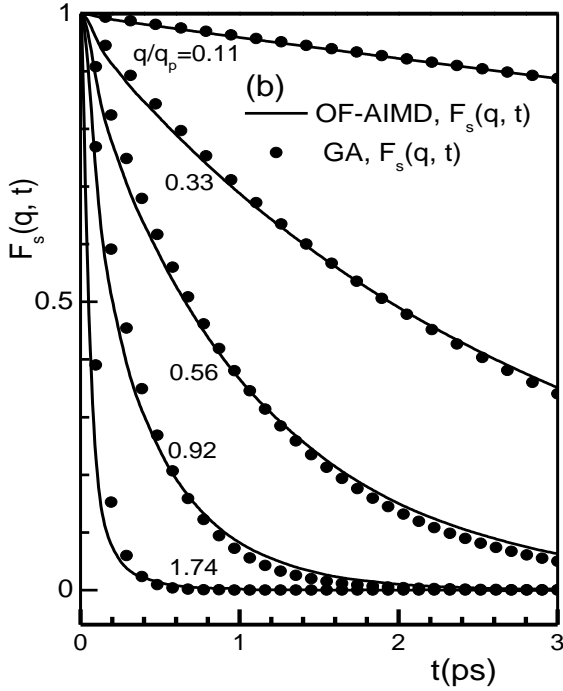
to compute experimental  $D$  by using experimental viscosity [30],  $\eta$  and main peak position,  $r_p$  of experimental  $g(r)$  [26]. Using the experimental values  $\eta=4.22 \text{ GPa ps}$ ,  $r_p=2.60 \text{ \AA}$  we get  $D=0.37 \text{ \AA}^2 ps^{-1}$ , which agrees well with our result,  $D=0.40 \pm 0.01 \text{ \AA}^2 ps^{-1}$  than the KS-AIMD result,  $D_{KS-AIMD}=0.27 \pm 0.02 \text{ \AA}^2 ps^{-1}$  [10].

The self-intermediate scattering function  $F_s(q, t)$ , delivers the most complete information about the single particle motion. This is related to the single particle dynamics, from the long wavelength (Hydrodynamic) limit ( $q \rightarrow 0$ ) to the short wavelength (independent particle) limit ( $q \rightarrow \infty$ ). In the present simulations, this magnitude has been defined as [3, 4],

$$F_s(q, t) = \frac{1}{N} \langle \sum_{j=1}^N \exp [i\vec{q} \cdot \vec{R}_j(t + t_0)] \exp [-i\vec{q} \cdot \vec{R}_j(t_0)] \rangle > \dots\dots\dots(12)$$

The well-known Gaussian approximation (GA) for  $F_s(q, t)$  is

$$F_s(q, t) = e^{-Dq^2t}, \dots\dots\dots(13)$$

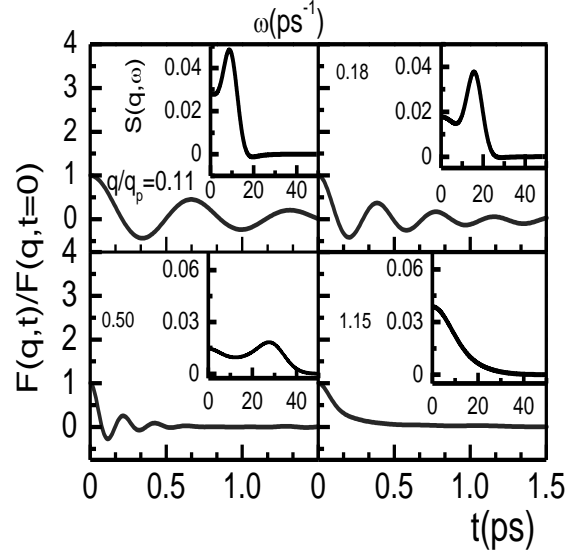


**Fig. 2: (b)**  $F_s(q, t)$  for different  $q/q_p$  values of liquid Pd at  $T=1853K$ .

where,  $D$  denotes self-diffusion [27]. Fig. 2(b) shows the self-intermediate scattering function,  $F_s(q, t)$  for several  $q/q_p$  values for l-Pd. Here the solid lines represent the OF-AIMD  $F_s(q, t)$  as defined in Eqn. (12) and, the filled circles represent the Gaussian approximation of  $F_s(q, t)$  as given by Eqn. (13). Fig. 2(b) illustrates that,  $F_s(q, t)$  decreases monotonically and non-linearly as a function of  $t$  and, the decrement gets faster as the magnitude of  $q/q_p$  enhances. This trend is apparently like that of simple liquid metals near triple points [3, 4, 10, 27]. Fig. 2(b) also shows that, equation (12) and equation (13) merge completely at small  $q/q_p$  values. This implies that,  $F_s(q, t)$  is mostly controlled by  $D$ . Some deviation near small  $t$  shows the shortcoming of the Gaussian approximation.

### 3.4 Collective Dynamics

The intermediate scattering function,  $F(q, t)$  is a density-density correlation function. It yields full information regarding the collective dynamics due to density fluctuation. It is defined as [3, 4]



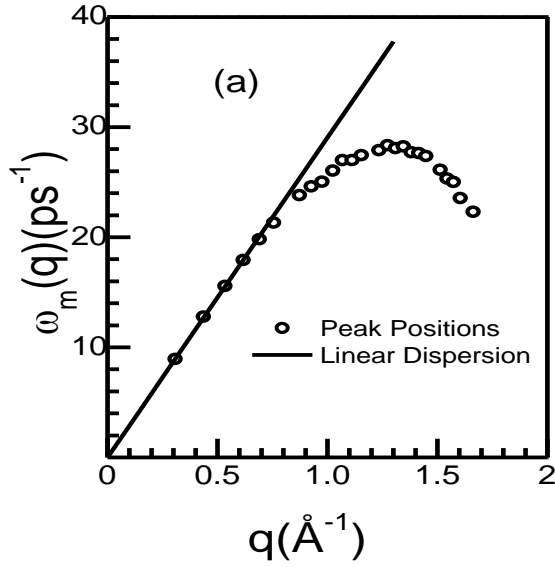
**Fig. 3.:** Normalized  $F(q, t)$  for different  $q/q_p$  values of liquid Pd at  $T=1853K$ . The inset represent the corresponding dynamic structure factor,  $S(q, \omega)$ .

$$F(q, t) = \left(\frac{1}{N}\right) \left\langle \sum_{j=1}^N \exp [i\vec{q} \cdot \vec{R}_j(t + t_0)] \sum_{l=1}^N \exp [-i\vec{q} \cdot \vec{R}_l(t_0)] \right\rangle \dots (14)$$

where,  $N$  is the total number of particles and  $\vec{R}_j(t)$  is the position of the  $j$ th ion at time  $t$ . Results for  $F(q, t)$  from the present OF-AIMD simulations are shown in Fig.3. Our OF-AIMD calculated,  $F(q, t)$  exhibits oscillatory behavior which persists approximately up to  $q \approx 0.73q_p$  and the amplitude of the oscillations being stronger for the smaller  $q$  values. This typical feature is seen in both computer simulations and theoretical models [3, 4, 10, 27, 31] study for liquid metals near melting.

The dynamic structure factor  $S(q, \omega)$  is closely related to the  $F(q, t)$  and, it is derived from the Fourier transform of the intermediate scattering function with respect to time. Here, an appropriate window is used to smooth out truncation effects [27, 31]. Fig. 3 illustrates  $S(q, \omega)$  where it shows distinct side peaks as an indication for collective density excitation for small  $q/q_p$  values. Practically, it is seen up to  $q \approx 0.73q_p$ .  $S(q, \omega)$  exhibits a decaying tail, and high frequency peaks in the hydrodynamic limit ( $q \rightarrow 0$ ); these peaks do not exist in the large  $\omega$ -region. A dispersion relation of the density fluctuation is obtained by plotting positions of the side peak,  $\omega_m(q)$ , for different  $q$  values (Fig.

4(a)) which gives an estimate of the adiabatic sound velocity,  $c_s(q)$ .



**Fig. 4: (a)** Dispersion relation for liquid metal Pd at  $T=1853K$ .

The slope of this dispersion relation curve in the limit  $q \rightarrow 0$  gives OF-AIMD bulk sound velocity,  $c_s = 2906 \pm 25$  m/s. We do not have any experimental  $c_s$  at 1853K, instead we have a calculated value  $c_s = 2657$  m/s [32] for Pd at melting. The AIMD study of González *et al.* [10] have reported a value  $c_s = 3450 \pm 150$  m/s which is almost 15% larger than that of our OF-AIMD result.

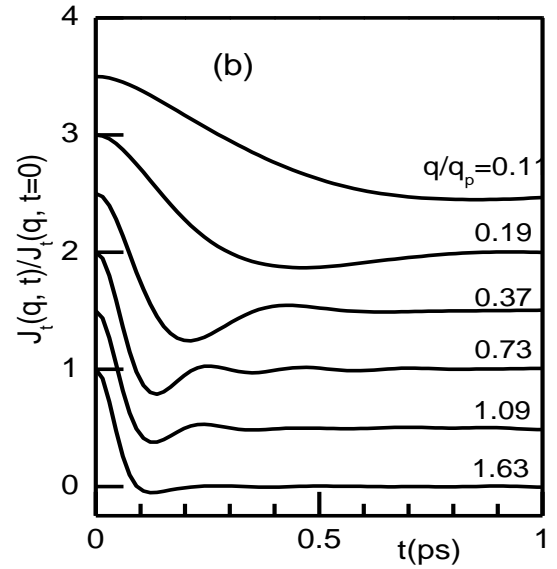
Another fascinating dynamical magnitude is the transverse current correlation function,  $J_t(q, t)$  which is not linked with any measurable quantity and can only be found through MD simulations. It carries information about the shear modes, and is defined as [27, 31],

$$J_t(q, t) = \frac{1}{N} \langle J_x^*(\vec{q}, 0) J_x(\vec{q}, t) \rangle \dots \dots \dots (15)$$

where,  $J_x(q, t) = \sum_{j=1}^N v_x^j(t) \exp[i\vec{q} \cdot \vec{R}_j(t)]$  is the transverse current. The shape of  $J_t(q, t)$  evolves from a Gaussian, in both  $q$  and  $t$ . For the free-particle limit ( $q \rightarrow \infty$ ), toward a Gaussian in  $q$  and exponential in  $t$  for the hydrodynamic limit ( $q \rightarrow 0$ ) [27, 31], *i.e*

$$J_t(q \rightarrow 0, t) = \frac{1}{\beta m} \exp \left[ -\frac{q^2(\eta|t|)}{m\rho} \right] \dots \dots \dots (16)$$

where,  $\eta$  is the shear viscosity. For intermediate  $q/q_p$  -values,  $J_t(q, t)$  exhibits a more complicated behavior, as shown in Fig. 4(b). We see that for small  $q/q_p$  values the corresponding  $J_t(q, t)$  decrease slowly but it becomes faster with increasing  $q/q_p$  values. Note that for the smallest  $q$  value reached by the simulation,  $q = 0.308 \text{ \AA}^{-1}$ , the corresponding  $J_t(q, t)$  takes on negative values, which by equation (16) means that it is already beyond the hydrodynamic regime. From the results for  $J_t(q, t)$  we can readily obtain the shear viscosity coefficient,  $\eta$  as follows [27, 33, 34].



**Fig. 4: (b)**  $J_t(q, t)$  for different  $q/q_p$  values of liquid Pd at  $T=1853K$ .

The memory function demonstration of  $J_t(q, t)$  is defined as [27, 31],

$$\tilde{J}_t(\mathbf{q}, \mathbf{z}) = \frac{1}{\beta m} \left[ \mathbf{z} + \frac{q^2}{m\rho} \tilde{\eta}(\mathbf{q}, \mathbf{z}) \right]^{-1} \dots \dots \dots (16)$$

where,  $\tilde{\eta}(\mathbf{q}, \mathbf{z})$  denotes a generalized shear viscosity coefficient and the tilde represents the Laplace transform. The area under the normalized  $J_t(q, t)$ , gives  $\beta m \tilde{J}_t(\mathbf{q}, \mathbf{z} = \mathbf{0})$ , from which values for  $\tilde{\eta}(\mathbf{q}, \mathbf{z} = \mathbf{0})$  can be obtained which, when extrapolated to  $q = 0$ , provides the usual shear viscosity coefficient,  $\eta$ . The OF-AIMD result for  $\eta$  is  $4.07 \pm 0.50$  GPa ps which is very close to the CMD simulated value of  $4.01 \pm 0.48$  GPa ps by Alemany *et al.* [6]. The experimental value for  $\eta$  is  $4.22 \pm 0.15$  GPa ps [30] which is also very close to



our OF-AIMD result. Our OF-AIMD result agrees well with the KS-AIMD result,  $\eta_{KS-AIMD} = 4.57 \pm 0.15 \text{ GPa ps}$  [10]. The other CMD simulation methods yielded reduced  $\eta$  values, *i.e.*  $3.68 \pm 0.48 \text{ GPa ps}$  [7],  $2.91 \pm 0.86 \text{ GPa ps}$  [9] and  $2.69 \text{ GPa ps}$  [5].

#### 4. CONCLUSION

Several static and dynamic properties of liquid Pd are studied in this article using OF-AIMD simulation technique at  $T=1853\text{K}$ . Simulated static structure factor and the pair distribution function are found to be good in agreement with the experimental [26] and other simulated data. The self-diffusion coefficient, obtained from the single particle dynamics, and the shear viscosity, derived from the collective dynamics of density fluctuation, also agree well with available data [5-7, 9, 10, 30]. The evaluated dynamic structure factors exhibit clear side peaks indicate collective excitation from which the velocity of sound is evaluated. Finally, we can conclude that, the engaged simulation method is a very good technique to determine the interesting static and dynamic properties of liquid Pd from the microscopic information at the atomic level.

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#### REFERENCES

[1] Hohenberg P. and Kohn W. Inhomogeneous Electron Gas. *Phys. Rev.*, **136**, B864-B871 (1964).  
 [2] Kohn W. and Sham L. J. Self-consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.*, **140**, A1133- A1138 (1965).  
 [3] González D. J., González L. E., López J. M. and Stott M. J. Orbital free ab initio molecular dynamics study of liquid Al near melting. *J. Chem. Phys.*, **115**, 2373-2376 (2001).  
 [4] Bhuiyan G. M., González L. E. and González D. J. Orbital free ab initio molecular dynamics simulation study of some static and dynamic properties of liquid noble metals. *Condens. Matter Phys.*, **15:3**, 33604:1-19 (2012).  
 [5] Çoruh A. Molecular-dynamics Investigation of the Dynamic Properties of Pd and Al Metals, And

Their Alloys. Ph. D. Thesis, Department of Physics, Middle East Technical University (2003).  
 [6] Alemany M. M. G., Rey C. and Galleogo L. J. Transport coefficients of liquid transition metals: A computer simulation study using the embedded atom model. *J. Chem. Phys.*, **109**, 5175-5176 (1998).  
 [7] Alemany M. M. G., Diéguez O., Rey C. and Galleogo L. J. Molecular-dynamics study of the dynamic properties of fcc transition and simple metals in the liquid phase using the second-moment approximation to the tight-binding method. *Phys. Rev. B*, **60**, 9208-9211 (1999).  
 [8] Bhuiyan G. M., Silbert M. and Stott M. J. Structure and thermodynamics properties of liquid transition metals. *Phys. Rev. B*, **53(2)**, 636-645(1996).  
 [9] Kart S. Ö., Tomak M., Uludoğan M., and Çağın T. Liquid properties of Pd-Ni alloys. *J. Non-Crys. Solids*, **337**, 101-108 (2004).  
 [10] González L. E., González D. J., Molla M. R., Ahmed A. Z. Ziauddin. and Bhuiyan G. M. Ab-initio study of several static and dynamic properties of liquid palladium and platinum. *EPJ Web of Conferences*, **151**, 03002:1-7 (2017).  
 [11] Mei J. and Davenport J. W. Molecular-dynamics study of self-diffusion in liquid transition metals. *Phys. Rev. B*, **42**, 9682-9684(1990).  
 [12] Rio B. G del. Dynamic Properties of Liquid Metals and their Free surface with first Principles Molecular Dynamics. PhD Thesis, Departamento de Fisica Teorica, Universidad de valladolid, 47011 Valladolid, Spain (2017).  
 [13] Molla M. R., Ahmed A. Z. Ziauddin, Hossain M. A. and Bhuiyan G. M. Static and dynamic properties of liquid Fe: An OF-AIMD simulation study. *Physica B: Cond. Mat.*, **567**, 129-137 (2019).  
 [14] Molla M. R., Ahmed A. Z. Ziauddin, Sarker H., Bhuiyan G. M., González L. E. and González D. J. Static and dynamic properties of liquid Zn, Cd and Hg divalent metals: An orbital free ab-initio molecular study. *J. Non-Crys. Solids*, **406**, 45-53 (2014).  
 [15] Bhuiyan G. M., González L. E. and González D. J. An Orbital-free Molecular Dynamics Study of Static and Dynamic Properties of Liquid Sn. *Euro. Phys. J. Web of Conferences*, **15**, 01011:1-4 (2011).  
 [16] Moriarty J. A. Density-functional formulation of the generalized pseudopotential theory, II. *Phys. Rev. B*, **26**, 1754-1780 (1982).

- [17] Moriarty J. A. Density-functional formulation of the generalized pseudopotential theory, III. Transition-metal interatomic potentials. *Phys. Rev. B*, **28**, 3199-3231 (1988).
- [18] Moriarty J. A. Analytic representation of multi-ion interatomic potentials in transition metals. *Phys. Rev. B*, **42**, 1609-1628 (1990).
- [19] Gelatt C. D., Ehrenreich Jr. H. and Watson R. E. Renormalized atoms: Cohesion in transition metals. *Phys. Rev. B*, **15**, 1613-1628 (1977).
- [20] Phuong L. Do., Pasturel A., Manh D. Nguyen. Effect of s-d hybridization on interatomic pair potentials of the 3d liquid transition metals. *J. Phys.: Condens. Matter*, **5**, 1901-1918 (1993).
- [21] Caldeín L., González D. J., González L. E. and Lopez J. M. Structural, dynamic, and electronic properties of liquid tin: An ab initio molecular dynamics study. *J. Chem. Phys.*, **129**, 194506:1-12 (2008).
- [22] Trouiller N. and Martins J. L. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B*, **43**, 1993-2006 (1991).
- [23] Caldeín L., González L. E. and González D. J. First-principles study of the layering at the free liquid Sn surface. *Phys. Rev. B* **80**, 115403:1-7 (2009).
- [24] Itami T., Munejiri S., Masaki T., Aoki H., Ishil Y., Kamiyama T., Senda Y., Shimojo F. and Hoshino K. Structure of liquid Sn over a wide temperature range from neutron scattering experiments and first-principles molecular dynamics simulation: A comparison to liquid Pb. *Phys. Rev. B*, **67**, 064201:1-12 (2003).
- [25] Abarenkov I. V. and Heine V. The model potential for positive ions. *Phil. Mag.*, **12**, 529-537 (1965).
- [26] Waseda Y. The Structure of Non-crystalline Materials. *McGraw-Hill Pub. Co.*, New York (1980).
- [27] Balucani U. and Zoppi M. Dynamics of the Liquid State. *Clarendon press*, Oxford, (1994).
- [28] Molla M. R. Study of the bulk properties of liquid transition metals. PhD Thesis, Department of Theoretical Physics, University of Dhaka (2016).
- [29] Landau L. D. Fluid Mechanics. *Pergamon*, New York (1987).
- [30] Iida T. and Guthrie R. I. L. The Thermophysical Properties of Metallic Liquids. *Oxford University Press*, Oxford (1993).
- [31] González D. J., González L. E. López J. M. and Stott M. J. Dynamical properties of liquid Al near melting: An orbital-free molecular dynamics study. *Phys. Rev. B*, **65**, 184201:1-13 (2002).
- [32] Sidney B. Correlation between surface tension, density, and sound velocity of liquid metals. *J. Colloid and Interface Science*, **302**, 312-314 (2006).
- [33] Palmer B. J. Transverse-current autocorrelation function calculations of the shear viscosity of molecular liquids. *Phys. Rev. E*, **49**, 359-366 (1994).
- [34] Balucani U., Brodholt J. P., Jedlovsky P. and Vallauri R. Viscosity of liquid water from computer simulations with a polarizable potential model. *Phys. Rev. E*, **62**, 2971-2973 (2000).