

Self-Diffusion Coefficients in Liquid Ag Using the Embedded Atom Model Based Effective Pair Potentials

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Abstract

We present the dynamical properties of liquid Ag at different temperatures, using the Mishin and Doyoma-Kagure version of the Embedded Atom Model (EAM) potentials. They have been evaluated within the framework of the mode-coupling theory, using a self-consistent scheme that uses as input data only the static structure functions and the interatomic pair potentials of the liquid Ag. We have computed single-particle and collective time dependent properties of liquid Ag, and thereby calculated its self-diffusion constants. We have also discussed our results comparing with both experimental data and results of molecular dynamic simulation.

Key Words: Dynamic Properties, Self-diffusion

1. Introduction

Diffusion is the transport of mass from one region to another on an atomic scale. Diffusivities in the liquid state are much higher than diffusivities in solid state. In the case of metals, diffusivities in the two states differ by a factor of 100 to 1000. The high atomic mobility of most metals just above their melting temperatures, with diffusivities of the order of $10^{-9}\text{m}^2\text{s}^{-1}$, is one of the most characteristic properties of liquids.

Unfortunately, there are problems associated with experimental work relating to diffusion measurements in liquid metals. First, experimental data for the self-diffusivities of liquid metals are relatively scanty, mainly because of a lack of specific radio-isotopes. At present, it would appear that experimental self diffusivity data are only available for the twelve or thirteen liquid metals. For a clear understanding of those phenomena related to diffusion, a study of self-diffusion in liquid metals is of critical importance. A second difficulty with diffusion is that while many experimental investigations have been carried out on solute diffusivities in liquid metals, the data are scarcely of sufficient accuracy. Similarly, while a variety of expressions describing solute diffusivities has been proposed, most of these equations are, unfortunately, unreliable in predicting solute diffusivities in many important liquid metal systems [1].

The study of diffusion in liquid metals is of grate interest because of various scientific and technological reasons. The knowledge of diffusion coefficients plays important role in design of metallurgical and solidification process such as in casting industry. The transport properties of liquids together with structural thermodynamic information can provide experimental basis for theories of the liquid state [2].

The Embedded Atom Model (EAM) based empirical potentials are extremely useful for the investigation of liquid properties of metals such as structure, thermodynamic and atomic transport properties. There are several EAM versions, which are different functions involved and the parameterization methods applied [3, 4]. Investigation of atomic transport properties of liquid metals based on EAM potential has been

reported lately. However, experimental data on the self-diffusion coefficients of liquid metals are available on few metals. It has been focused on the atomic transport properties of liquid Ag in this paper. We have used two versions of the EAM, originally proposed by Mishin *et al.* (M-EAM) [5] and Doyama-Kagure (DK-EAM) [6]. These EAM versions were successfully used to calculate the structure and thermodynamic properties of liquid fcc metals [7].

In this work, these models have also been applied to calculate the self-diffusion coefficients of liquid Ag at various temperatures. Using the effective pair potentials, the Variational Modified Hypernetted Chain (VMHNC) approximation [8] have been carried out to compute both single-particle and collective time-dependent properties of liquid Ag. This paper also dedicated to test the capability of the effective pair potential approximation based on EAM for describing the atomic dynamic in liquid Ag.

To calculate self-diffusion coefficients for liquid metals, the theory for the dynamical structural properties can be used. As we mentioned in our former work [9], this theory gives good agreement compared with experimental predictions whereas different experiments yield different data and the experimental errors are relatively large. On the other hand, many authors have calculated self-diffusion coefficients by using different molecular dynamic modeling.

This paper is organized as follows. In Sec. 2, we describe the theory used for the calculation of the dynamic properties. In Sec. 3, we present the results when this theory is applied to liquid Ag at various temperatures. Finally, Sec. 4 summarizes the main results of the work along with a few concluding remarks.

2. Theory

The self-diffusion coefficients of the interested liquid metal systems can be calculated using time-dependent correlation functions [10] known as the Green-Kubo (G-K) relation in which the coefficient is given as the time integral of a corresponding time correlation function

$$D = \frac{k_B T}{m} \int_0^\infty Z(t) dt, \quad (1)$$

where $Z(t) = \langle \mathbf{v}_1(t) \mathbf{v}_1(0) \rangle / \langle v_1^2 \rangle$ is the normalized velocity autocorrelation function and, k_B is the Boltzmann constant, T denotes the temperature, and m is the mass of particles. $Z(t)$ is a measure of projection of the particle velocity at time t on to its initial value, averaged over all initial conditions. Also the coefficient can be computed by Einstein (E) relation

$$D = \lim_{t \rightarrow \infty} \frac{\delta r^2(t)}{6t}, \quad (2)$$

where $\delta r^2(t)$ defined with the mean square displacement of a tagged particle. These two different diffusion functions are related each other by

$$\delta r^2(t) = \frac{6k_B T}{m} \int_0^t d\tau (t - \tau) Z(\tau). \quad (3)$$

The memory function of normalized velocity autocorrelation function, $K(t)$, is defined by the following Volterra-type equation

$$\dot{Z}(\tau) = - \int_0^\tau K(t - t') Z(t') dt', \quad (4)$$

where the dot means time derivative of normalized velocity autocorrelation function. The memory function may be split into two contributions [11, 12]

$$K(t) = K_B(t) + K_{MC}(t), \quad (5)$$

which represent two distinct dynamical regimes in the atomic dynamics of a liquid. The first term comprises all the fast decay channels. It is supposed to represent the effect of a binary collision between a tagged particle and another one from its environment whereas the second term, the mode-coupling contribution, incorporates

the contribution from the collective process associated with repeated collisions, the ring collisions. At very short times the memory function is well described by $K_B(t)$ only, moreover both $K(t)$ and $K_B(t)$ have the same initial value (Ω_0^2) and initial time decay (τ_D)

$$K(0) = K_B(0) = \Omega_0^2 \equiv \frac{\rho}{3m} \int \nabla^2 \phi(r) g(r) dr, \quad (6)$$

and

$$\tau_D = \left[\frac{|\dot{K}(0)|}{2K(0)} \right]^{-\frac{1}{2}}, \quad (7)$$

where Ω_0^2 is the Einstein frequency which, as shown in equation (6), can be written in terms of the interatomic pair potential, $\phi(r)$, and the pair distribution function, $g(r)$ of the liquid with number density ρ . As the detailed features of the binary dynamics of systems with continuous potentials are rather poorly known, we resort to a semi-phenomenological approximation by writing [13]

$$K_B(t) = \Omega_0^2 \sec h^2(t/\tau_D), \quad (8)$$

which besides of correct short time behavior, also allows the computation of $K_B(t)$ from the static structural function only. The inclusion of a slowly decaying time tail in memory function is known to be an essential ingredient for the correct description of the dynamics of a tagged particle in fluid. In principle, coupling to several modes, should be considered such as density-density coupling, density-longitudinal current coupling and density-transversal current coupling but for the density/temperature range considered in this work, the most important contribution arises from density-density coupling as we already mentioned. Restricting the mode-coupling component to the density-density coupling term [14]

$$K_{MC}(t) = \frac{\rho k_B T}{24\pi^3 m} \int d\mathbf{k} k^2 c^2 [F_s(k, t) F(k, t) - F_{sB}(k, t) F_B(k, t)]. \quad (9)$$

Here, $c(k)$ denotes the direct correlation function of the liquid. $F(k, t)$ is the intermediate scattering function which is obtained by using viscoelastic model and $F_s(k, t)$ is its self part whereas $F_B(k, t)$ and $F_{sB}(k, t)$ shows binary part of $F(k, t)$ and $F_s(k, t)$, respectively. The binary part of the self-intermediate scattering function as its value for free particles and its self part are given by

$$F_{sB}(k, t) = F_o(k, t) \equiv \exp \left[-\frac{k_B T}{2m} k^2 t^2 \right]. \quad (10)$$

By assuming that the ratio between $F(k, t)$ and its binary part could be approximated by the ratio between their corresponding self parts, the following expression was proposed for $F_B(k, t)$

$$F_B(k, t) = \frac{F_o(k, t)}{F_s(k, t)} F(k, t), \quad (11)$$

where $F_{sB}(k, t) = F_o(k, t)$. The final expression for the mode-coupling part of the memory function of the normalized velocity autocorrelation function then becomes

$$K_{MC}(t) = \frac{\rho k_B T}{24\pi^3 m} \int d\mathbf{k} k^2 c^2 \left[F_s(k, t) - \frac{F_o^2(k, t)}{F_s(k, t)} \right] F(k, t). \quad (12)$$

As already mentioned, the authors [15, 16, 17] have calculated the dynamical properties of liquid alkali metals by using, basically the same coupling term as given in equation (13). Finally, in the case of $F_s(k, t)$ we have used Gaussian approximation

$$F_s(t) = \exp \left[-\frac{1}{6} k^2 \delta^2(t) \right], \quad (13)$$

which gives correct results for both small and large wavevectors.

We propose here self-consistent calculation of the memory function itself, by using the following procedure. We start with some estimation for the mode-coupling component of the memory function, for instance, $K_{MC}(t) = 0$. Using known values of $K_B(t)$ and equation (5) a total memory function is obtained which, when taken equation (4), gives a normalized velocity autocorrelation function and through equation (3) leads to the mean square displacement. Now, evaluation of integral given in equation (12) leads to new estimate for the mode-coupling component of the memory function. Finally, this loop iterated until self-consistency is achieved between the initial and final total memory function, $K(t)$, [18].

3. Results and Discussion

We have applied the theoretical formalism to study the dynamic properties of liquid Ag at various temperatures. The input data required by the theory are both the interatomic pair potential and its derivatives as well as the liquid static structural properties. We have used the interatomic pair potential which is derived from EAM-related two versions: M-EAM and DK-EAM. The parameterization data sets of these models are obtained from Ref. [3]. When it is used in conjunction with VMHNC theory of liquids has proved to be highly accurate for the calculation of liquid static structure and thermodynamic properties. In Table 1, we give the input data which are densities and temperatures [1, 19].

Table 1. The input parameters for liquid Ag.

T (K)	1273	1423	1600	1700	2100
ρ (atoms/Å ³)	0.0517	0.0509	0.0502	0.0497	0.0477

Using the EAM based effective pair potentials, the VMHNC approximation is employed to calculate the liquid state pair distribution functions, $g(r)$, and static structure factors, $S(k)$. In these calculations Zerah's algorithm is used to solve Ornstein-Zernike (O-Z) equation. The O-Z equation is the starting point of almost all integral theories of liquids for an isotropic, homogenous system. The calculated $S(k)$ and $g(r)$ for liquid Ag are shown along with the experimental data of Waseda in Figures 1a-b, respectively.

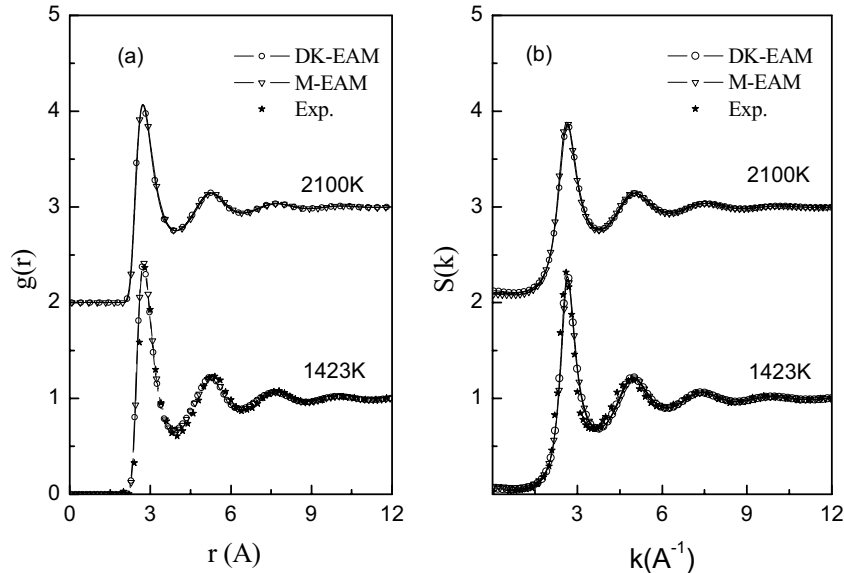


Figure 1. (a) Pair distribution functions and (b) static structure factors for liquid Ag.

We have applied the iterative scheme described at above. We found that numbers of 3-5 iterations are enough to achieve self-consistency in memory function. The results are shown in Figure 2 where we plotted theoretical total memory function, $K(t)$, along with its two components; binary and mode-coupling parts. In the same figure it is clearly shown that the memory functions are only plotted at two temperatures from

inside of those studied temperatures. The binary parts dominates the behavior of $K(t)$ for $t \leq 2\tau_D$. The mode-coupling part completely determines the shape of $K(t)$ for longer times.

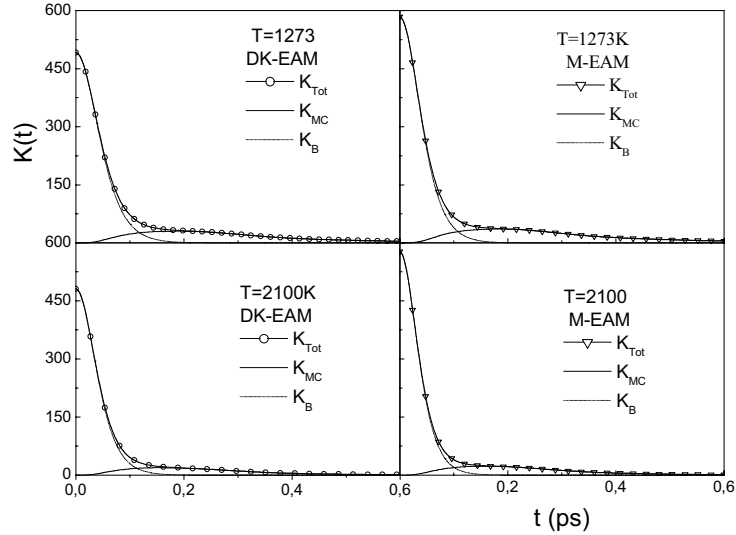


Figure 2. Memory functions for liquid Ag.

Normalized velocity autocorrelation function obtained from theoretical $K(t)$ are shown Figure 3 where we have calculated $Z(t)$ within self-consistency procedure. Also in this figure inset shows first minima of $Z(t)$. Figure 3 shows that $Z(t)$ has any weak oscillations and, rapidly goes to zero for all studied temperatures in this paper. It is clear that initial and final velocities of a single-particle expected to be completely decorrelated as from shorter times for liquid Ag.

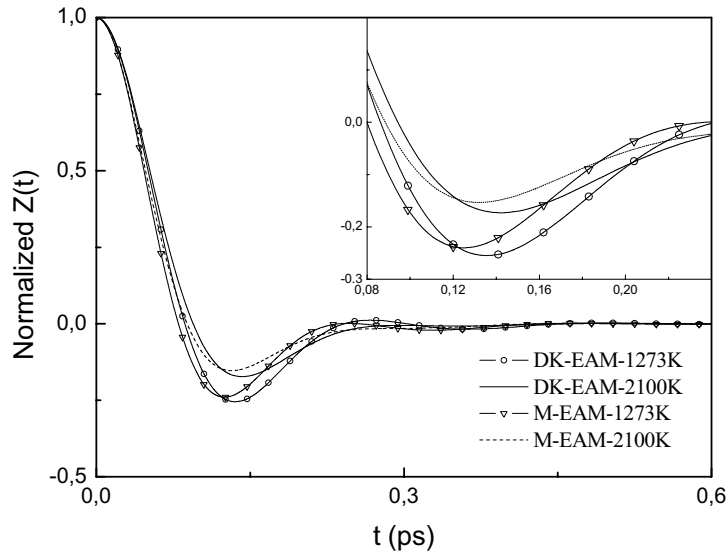


Figure 3. Normalized velocity autocorrelation functions for liquid Ag.

The Mean Square Displacements (MSD) were calculated as a function of temperature 1273K to 2100K for liquid Ag and it is plotted in Figure 4. The MSDs vary linearly with time at all temperatures in both EAM based effective pair potentials.

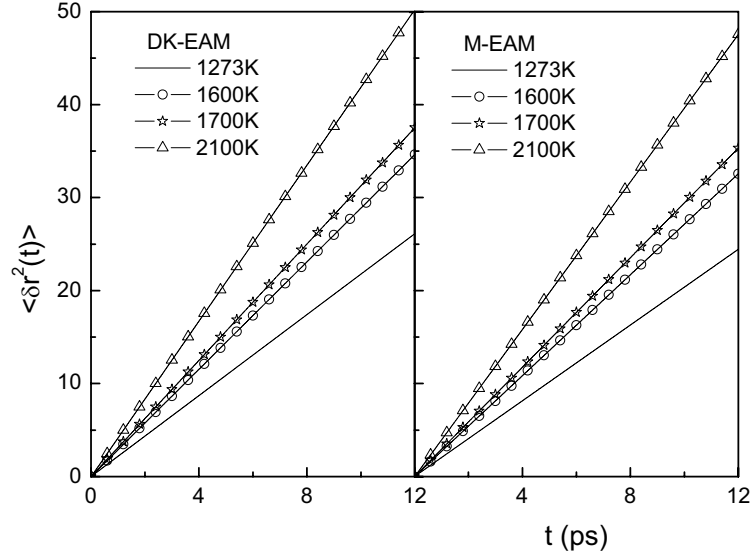


Figure 4. Mean square displacements for liquid Ag at various temperatures.

The results obtained for the self-diffusion coefficients, D , are shown in Table 2 for liquid Ag compared with both experimental data [19] and the other works [2, 20]. Our computed values also agree with experiment for the state at near melting. However, the M-EAM value is closer to experiment than the other EAM version. On the other hand, there is no experimental data at 2100 K to the best of our knowledge to compare our results of self-diffusion coefficient. It can be seen that our value at 1273 K is closer to experiment than those obtained by Linearized Weeks-Chandler-Anderson (LWCA) approximation.

Table 2. Self-diffusion coefficients.

	$D(A^2/ps)$			
	T=1273K		T=2100K	
	DK-EAM	M-EAM	DK-EAM	M-EAM
Present work (G-K)	0.3628	0.3395	0.6513	0.6159
Present work (E)	0.3629	0.3396	0.6971	0.6598
Protopapas	0.2858		1.0234	
LWCA	0.1030		0.7170	
Akhter	-		1.3290	
Exp.	0.2810		-	

Finally, the calculated self-diffusion coefficients for both EAM based effective pair potentials are plotted as a function of temperature in Figure 5. It is seen that our computed values are rather slowly increasing compared with the others [2, 20].

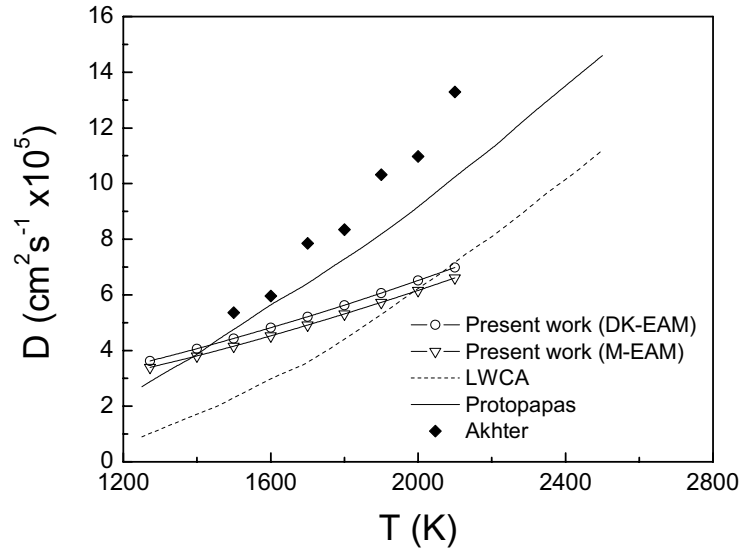


Figure 5. The self-diffusion coefficients.

4. Conclusions

We checked the reliability of the M-EAM and DK-EAM for the described dynamic properties of liquid Ag by computing the self-diffusion coefficients. It is shown that VMHNC calculations based on two different EAM potentials are capable of describing the dynamic properties of liquid Ag. On the theoretical side, we have shown that a simplified mode-coupling approach is able to reproduce rather well several features of single-particle motion, including both the ordinary and k-dependent diffusion coefficient. There is general agreement between the computed values of D with other theoretical results and experimental data.

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References

- [1] T. Iida and R. I. L Guthrie, *The Physical Properties of Liquid Metals*, (Oxford Univ. Press, New York, 1993).
- [2] J. I. Akhter, E. Ahmed, and M. Ahmad, *Mater. Chem. and Phys.*, **93**, (2005), 504.
- [3] U. Domekeli, MSc Thesis, Department of Physics, Graduate School of Natural and Applied Sciences, Edirne, Turkey, 2003.
- [4] S.S. Dalgic, S. Dalgic, and U. Domekeli, *J. Optoelectron. Adv. Mater.*, **5**, (2003), 1263.
- [5] Y. Mishin, M. J. Mehl, D. A. Papaconstantopoulos, A. F. Voter, and J. D. Kress, *Phys. Rev. B*, **63**, (2001), 224106.
- [6] M. Doyama and Y. Kagure, *Comp. Mat. Sci.*, **14**, (1999), 80.
- [7] S. S. Dalgic and U. Domekeli, *to be published*.
- [8] Y. Rosenfeld, *J. Stat. Phys.*, **42**, (1986), 437.
- [9] S. Dalgic, M. Çolakogullari, and S. S. Dalgic, *J. Optoelectron. Adv. Mater.*, **7**, (2005), 1993.

- [10] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, (Academic Press, London, 1986).
- [11] A. Sjölander, in *Amorphous and Liquid Materials*, ed: E. Lüscher, G. Fritsch, and G. Jacucci, (Martinus Nijhoff, Dordrecht, 1987).
- [12] L. Sjögren and A. Sjölander, *J. Phys. C*, **12**, (1979), 4369.
- [13] U. Balucani, A. Torcini, and R. Vallauri, *Phys. Rev. A*, **46**, (1992), 2159; *Phys. Rev. A*, **47**, (1993), 3011.
- [14] L. Sjögren, *J. Phys. C*, **13**, (1980), 705.
- [15] L.E. Gonzalez, D.J. Gonzalez, M. Canales, *Z. Phys. B*, **100**, (1996), 601.
- [16] L. E. Gonzalez, D. J. Gonzalez, J. Casas, *J. Non-Cryst. Solids*, **312-314**, (2002), 158.
- [17] Y. Rosenfeld, *J. Stat. Phys.*, **42**, (1986), 437.
- [18] M. M. G. Alemany, J. Casas, C. Rey, L. E. Gonzalez, L. J. Gallego, *Phys. Rev. E*, **56**, (1997), 6818.
- [19] Y. Waseda, *The Structure of Non-Crystalline Materials*, (McGraw-Hill, New York, 1980).
- [20] A. Z. Ziauddin Ahmed and G. M. Bhuiyan, *J. Mod. Phys. B*, **16**, (2002), 3837.