

Structures and autocorrelation functions of liquid Al and Mg modelled via Lennard–Jones potential from molecular dynamics simulation

G A ADEBAYO^a, O AKINLADE^b and L A HUSSAIN^c

^aThe Abdus Salam International Centre for Theoretical Physics, Trieste, Italy

^bDepartment of Physics, University of Agriculture, Abeokuta, Nigeria

^cDepartment of Physics, University of Ibadan, Ibadan, Nigeria

E-mail: gadebayo@ictp.trieste.it

MS received 31 March 2004; revised 14 October 2004; accepted 17 November 2004

Abstract. The structures and autocorrelation functions of Al and Mg in the liquid state are investigated through the pair distribution function $g(r)$, the diffusion coefficients as well as the shear viscosity via the Green–Kubo and Einstein relations. From the structure and the Enskog relation we determined the frequency of collisions of atoms in the first shell of $g(r)$ in the systems. We also discovered that the packing fraction of Lennard–Jones liquids should be approximately half the reduced density value. This approximation is accurate to within 99%. The temperature dependence of the pair distribution function and the atomic mean square displacement are investigated by performing simulations at various experimental temperatures and corresponding densities. The structures of the systems are affected by temperature via movements of atoms in the first minimum of $g(r)$.

The Lennard–Jones model shows that density dependence of the shear viscosity is in agreement with what is expected of simple liquids in the range of investigated temperatures and densities. In the gas limit, the Stoke–Einstein relation $D\eta = K_B T/2\pi\sigma$ is grossly overestimated by Lennard–Jones model. This could not be attributed to deficiencies in the model, as other investigators using first principle method could not obtain the gas limit of the Stoke–Einstein relation.

Keywords. Structure of liquids; viscosity of liquids; simple liquids.

PACS No. 61.20.Ja

1. Introduction

Starting from the late fifties and in particular the last two decades, molecular dynamics simulation has become an important tool to study static and dynamical properties of materials. It therefore follows naturally that there should exist approximate model potentials to describe the interactions among the atoms constituting a system. However, all the models aim to improve our understanding of the properties and the physics of real materials. The key ingredients in molecular

dynamics simulations are the interatomic forces. The efficient *ab initio* method [1] requires large computing resources, driving up computational cost very rapidly. In other words, while it is possible to attain a high level of accuracy with the *ab initio* calculations and the family of embedded atom method or the glue model [2–8] these methods still remain computationally expensive and are not easy to implement.

The structural interaction of many-body potential functions poses difficulty in the systematic theoretical calculation of some properties of a material. This is partly due to the fact that information on surrounding atomic nuclei are needed in the computation of many-body potential. Currently, only simple empirical interaction schemes allow the study of very large systems. With molecular dynamics simulation that treats interactions as pair-wise additive, it is possible to describe the structure [9] and particle coefficients of homogenous simple systems. The method of molecular dynamics simulation makes it possible to compute the static and dynamical properties of classical systems using Newton's equation of motion. By analysing the positions and velocities it is possible to obtain information on the properties of a system studied. Structural and dynamic properties of materials are of importance to improve our knowledge on temperature dependence of their properties at high temperature. A study of temperature dependence of the properties of materials requires a proper investigation of atomic motions and electron excitation. However, it is possible to approximate the collective motion in a material using the Born–Oppenheimer approximation such that properties of interest can be studied using atomic motions. Many calculations have been carried out using simulations on different liquid metals [10–12].

The work of Rahman [13] gives scope for discussing the analogies and differences between the properties of simple liquid metals and liquified inert gases. However, there are very small differences between the structure of these two types of fluids [2]. On the other hand, the differences between the dynamic properties of rare gas liquids and simple liquid metals are appreciable, but not completely understood. The autocorrelation functions in liquid metals have more pronounced oscillations than those of inert gas liquids [3]. This difference can be attributed to the different softness of their potential function core [14]. In this work, the method of molecular dynamics (MD) simulation using the 12-6 Lennard–Jones potential has been utilized to investigate the structure and autocorrelation functions of simple liquids. The Lennard–Jones potential is an effective potential that describes the interaction between two uncharged molecules or atoms. The Lennard–Jones potential is mildly attractive when two uncharged molecules or atoms approach one another from a distance, but strongly repulsive when they approach too close.

The main features of the first shell in liquid Al and liquid Mg are studied by structural analysis of the shell, using the autocorrelation functions the diffusion coefficients and viscosity were calculated. A standard molecular dynamics simulation code (UNAABMD) with 864 interacting atoms in a fixed simulation box of length L was used to calculate the static structure and transport coefficients of Al and Mg in the liquid state. This code uses the Verlet algorithm in calculating the equation of motions of atoms in the system. This work is organized as follows: in §2 the method of simulation and some calculation methods are outlined, §§3 and 4 contain the results and discussions respectively, while in §5 the major conclusions of this study are provided along with figures and tables.

2. Computer simulations and method of calculations

Molecular dynamics simulations of systems consisting of 864 particles with masses equal to unity enclosed in simulation box with periodic boundary conditions were performed. Simulations were performed at different densities and temperatures above the melting points of the systems. In selecting working conditions, reduced densities, temperatures and time were chosen to conform with the standard way of selection, that is, $\rho^* = \rho\sigma^3$ and $T^* = K_B T/\epsilon$, while the unit of time is $\sigma\sqrt{m/\epsilon}$. Here, ρ is the density of the system, σ is the atomic diameter, T is the temperature, while K_B is taken as unity. The parameters K_B and ϵ are respectively, the Boltzmann's constant and the potential minimum of the Lennard-Jones potential. It should be noted that σ is in Angstrom, while ϵ and T are in Kelvin. This implies that the parameters with $*$ are in reduced units. The input parameters for the Lennard-Jones model are $\sigma = 2.62 \text{ \AA}$ and 2.88 \AA and $(\epsilon/K_B) = 4551.28 \text{ K}$ and 1111.76 K for Al and Mg respectively. These parameters are taken from [15,16]. Initially, particles in the systems were assigned corresponding cubic lattice configurations, while velocities were set to zero.

We have used the standard velocity Verlet algorithm [17] in the MD technique. Interaction is only allowed up to a cut-off distance $r_c = \frac{1}{2}L$, where L is the length of the simulation box. This is then shifted by adding a term E_{cut} such that the potential and the force are both zero at r_c . E_{cut} is the value of the potential at the cut-off radius r_c . A time step of $\Delta t = 0.005$ was used to attain thermal equilibrium in each system, and this time step is acceptable as long as it is greater than the relaxation time of the systems. Also the time step (0.005) has to be normalized with respect to a physical time as given above, which is decided by the physical length a particle travels and the velocity of the particle. Using the time-scale given above, a rough estimate of physical time used in our simulations corresponds to $\approx 22 \text{ ps}$ for Al and $\approx 46 \text{ ps}$ for Mg.

We will like to say at this point that, while it is convenient to normalize such quantities, it does not mean that the physical reality of atomic size, temperature, energy and time vanishes with normalization. In this case, the parameter σ is related to the size of the metallic atoms in question, i.e. Al and Mg and the cell size of the simulation is decided by this parameter. Similarly, the temperature of simulation (in units of K_B) is an important parameter.

Systems were allowed to run for a minimum of 3000 time steps before data on positions and velocities were collected. Structural calculations are obtained through the pair distribution function given by [18]

$$g(r) = \frac{V}{N} \left\langle \frac{\Delta N}{4\pi r^2 \Delta r} \right\rangle \quad (1)$$

which is an average over the simulation time steps at equilibrium. The volume of the simulation box with N particles is V , while ΔN represents particles in a shell within the region $r - (\Delta r/2)$ and $r + (\Delta r/2)$, where Δr is the shell thickness and $\Delta r \ll r$. Since r and Δr are measures of position or distance, r and Δr are in units of length. In many homogenous dense liquids, the packing fraction η_{liq} can be calculated via the relation

$$\eta_{\text{liq}} = \frac{4}{3} \frac{N}{V} \pi R^3. \quad (2)$$

We see immediately that this can also be written as

$$\eta_{\text{liq}} = \frac{1}{6} \pi \rho \sigma^3 \quad (3)$$

since it is possible to express the atomic radius R of an atom in terms of its atomic size σ . If we use the reduced units of Lennard–Jones fluids, then we see that in the above equation the quantity $\rho \sigma^3$ is the reduced density of a Lennard–Jones fluid. With this it is possible for us to write

$$\eta_{\text{liq}} = \frac{\pi \rho \sigma^3}{6} = \frac{\pi \rho^*}{6}. \quad (4)$$

A closer look at eq. (4) suggests that

$$\eta_{\text{liq}} \approx \frac{1}{2} \rho^*. \quad (5)$$

This implies that for Lennard–Jones liquids the packing fraction can roughly be estimated from the value of the reduced density. This approximation is accurate to within $98 \pm 0.94\%$. The influence of the softness of the Lennard–Jones potential is pronounced at higher packing fraction. From structural properties, specifically the pair distribution function, it is possible to obtain information on collision of atoms in the first shell of a simple liquid by estimating the Enskog (collision frequency) using the relation [19]

$$\tau = 4\rho r_{\text{max}}^2 g(r_{\text{max}}) (\pi K_{\text{B}} T / m)^{1/2}, \quad (6)$$

where r_{max} is the position of the first peak in the pair distribution function [2], K_{B} and m are taken as unity. The coordination number could be calculated using any of the standard equations, but we have used the expression [20]

$$c_n = 4\pi\rho \int_0^{r_m} r^2 g(r) dr, \quad (7)$$

where r_m is the first minimum in $g(r)$. By this choice, the first shell is defined to end at the first minimum in $g(r)$. The diffusion coefficient is calculated from the mean square displacements of the atoms [2]:

$$D = \lim_{t \rightarrow \infty} \frac{\langle x^2(t) \rangle + \langle y^2(t) \rangle + \langle z^2(t) \rangle}{6t}, \quad (8)$$

where $\langle x^2(t) \rangle$, $\langle y^2(t) \rangle$ and $\langle z^2(t) \rangle$ represent the mean square displacement of a particle in the three dimensions. It should be noted that these are calculated from the trajectories as double-average over atoms, i.e.,

$$\langle x^2(t) \rangle = \frac{1}{N \cdot N_\tau} \sum (x_i(t + \tau) - x_i(\tau))^2, \quad (9)$$

where N_τ represents the number of different time origin τ used in averaging. Analysis of the velocity autocorrelation function also gives the diffusion coefficients D . From the normalized velocity autocorrelation it is possible to obtain the dynamic behaviour of particles in liquid systems. Both these methods are used in our calculations. The velocity autocorrelation function is given as

$$c(t) = \langle v(t) \cdot v(0) \rangle. \quad (10)$$

The shear viscosity is calculated from the xy components of the shear stress autocorrelation function [21]

$$\eta = \frac{1}{K_B T} \int_0^\infty \langle \sigma_{xy}(0) \cdot \sigma_{xy}(t) \rangle dt, \quad (11)$$

where the (x - y plane) shear stress σ_{xy} is given as

$$\sigma_{xy} = \sum_{i=1}^N \left(m_i v_{xyi}^2 + \frac{1}{2} \sum_{i=1}^N \sum_{j>i}^{N-1} r_{ij} f_{ij}(r_{ij}) \right) \quad (12)$$

$$f_{ij}(r_{ij}) = -\frac{\partial V(r_{ij})}{\partial r}. \quad (13)$$

To keep the pressure of the simulating system constant at all times, experimental values of densities [20] were used.

3. Results

In table 1, the calculated structural information in the first shell of liquid Al at six different temperatures and corresponding reduced densities are presented. Positions (r_{\max}) of first peaks in the pair distribution function, the frequency of collisions calculated from the Enskog relation, and the calculated and the estimated packing fraction of Al at all investigated temperatures are presented in table 1. We calculated the liquid packing fraction η_{liq} from eq. (4), while as mentioned earlier

Table 1. Calculated liquid packing fraction and frequency of collisions of atoms in the first shell of liquid Al.

T (K)	ρ^*	r_{\max} (Å)	τ	η_{liq}	$\eta_{\text{est}} \approx 0.5\rho^*$	r_0	r_0/r_{\max}
943	0.950	2.716	58.34	0.4953	0.4730	2.1580	0.7946
1085	0.941	2.730	62.65	0.4896	0.4676	2.1691	0.7945
1132	0.930	2.735	63.45	0.4871	0.4652	2.1728	0.7944
1155	0.928	2.737	64.22	0.4797	0.4581	2.1746	0.7945
1270	0.916	2.749	67.29	0.4798	0.4512	2.1838	0.7944
1323	0.911	2.703	66.00	0.4769	0.4554	2.1881	0.8095

Table 2. Calculated liquid packing fraction and frequency of collisions of atoms in the first shell in liquid Mg.

T (K)	ρ^*	r_{\max} (Å)	τ	η_{liq}	$\eta_{\text{est}} \approx 0.5\rho^*$	r_0	r_0/r_{\max}
953	0.915	2.967	134.37	0.4790	0.4575	2.345	0.7904
1063	0.848	3.043	136.24	0.4440	0.4240	2.405	0.7905
1153	0.793	3.112	121.02	0.4153	0.3965	2.460	0.7904

Table 3. Calculated properties from autocorrelation functions of atoms in liquid Al.

T (K)	ρ^*	r_m (Å)	D	η	$D\eta$	$D\eta = \frac{K_B T}{2\pi\sigma}$
943	0.950	3.884	0.1174	3.4238	0.40195	0.0125866
1085	0.941	3.904	0.1099	1.8931	0.20805	0.0144819
1132	0.930	3.963	0.1087	2.6859	0.291957	0.0151076
1155	0.928	3.965	0.10953	2.4032	0.26322468	0.0154174
1270	0.916	3.931	0.1038	1.6479	0.17105	0.016948225
1323	0.911	3.939	0.1059	1.7834	0.18886	0.017658957

Table 4. Calculated properties from autocorrelation functions of atoms in liquid Mg.

T (K)	ρ^*	r_m (Å)	D	η	$D\eta$	$D\eta = \frac{K_B T}{2\pi\sigma}$
953	0.915	4.323	0.1303	2.323	0.3027	0.0475
1063	0.848	4.492	0.1127	1.082	0.1219	0.0530
1153	0.793	4.534	0.1077	0.442	0.0476	0.0575

the estimated packing fraction η_{est} of Lennard–Jones liquid is obtained from the approximation in eq. (5). At 943 K, the expected experimental value of the ratio of the position r_0 of minimum $g(r)$ to the position r_{\max} of maximum $g(r)$ is 0.82 [22], we determined this value at all investigated temperatures and found that the Lennard–Jones potential gives values in agreement with experiment. Table 2 contains the same information as in the first table, but for liquid Mg at experimental temperatures and densities. Although experimental value of the r_0/r_{\max} ratio was at 953 K, our simulation results show good agreement with this value at all temperatures. Tables 3 and 4 consist of autocorrelation functions of liquid Al and Mg respectively. For liquid Al, the temperature range is between 943 and 1323 K, while for Mg, the temperature range is between 953 and 1153 K. Temperatures and densities, the position r_m of the first minimum in the $g(r)$ the calculated diffusion coefficient and viscosity are given in tables 3 and 4. Using the Stoke–Einstein relation, we computed the product of the diffusion coefficient and the viscosity, as well as the value $D\eta$ from our simulation. The discrepancies noticed in the calculated Stoke–Einstein relation could be partly ascribed to the signature of the simplistic two-body potential approximation. Figure 1 gives the pair distribution function of

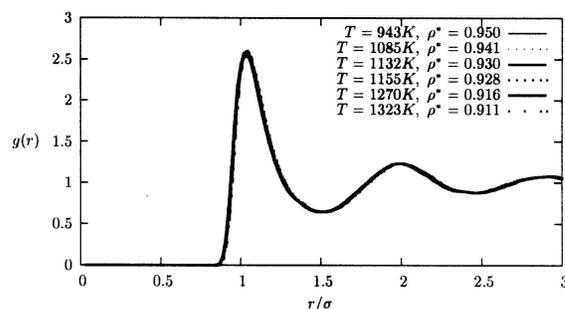


Figure 1. The six calculated pair distribution functions of Al from our simulations at different temperatures and corresponding densities.

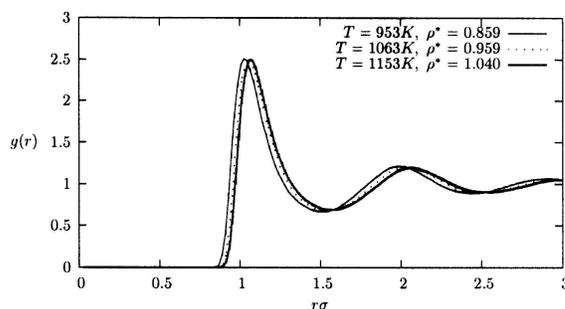


Figure 2. Calculated pair distribution functions of Mg at temperatures 953, 1063 and 1153 K and corresponding densities.

liquid Al in unit of σ . There is no appreciable difference in the static structure via the $g(r)$ of Al at all investigated temperatures. This is probably due to the fact that simulations are performed with values of densities that are close together.

The structure of Mg shows a slight difference in the $g(r)$ at higher temperature and lower density as shown in figure 2. This is manifested by a shift in the position r_{\max} of the first peak and results in lower packing of atoms in the first shell. A comparison is made between the simulated results and experimental data of Waseda [20]; these are presented in figures 3 and 4. In figure 3, the Lennard–Jones model underestimates the first peak in the $g(r)$, but the position of the first peak is predicted accurately to 2.716 ± 0.074 Å of experiment. However, the agreement between experiment and simulation is commendable after the first peak. In liquid Mg, it is observed that negative values appeared in the experimental data. However, there is a good agreement between experiment and simulation as r increases.

4. Discussions

With good choice of parametrization of the atomic size and potential of minimum ϵ , a potential model as simple as the Lennard–Jones is able to describe well the structures of some simple liquids such as Al and Mg. Both the diffusion coefficient

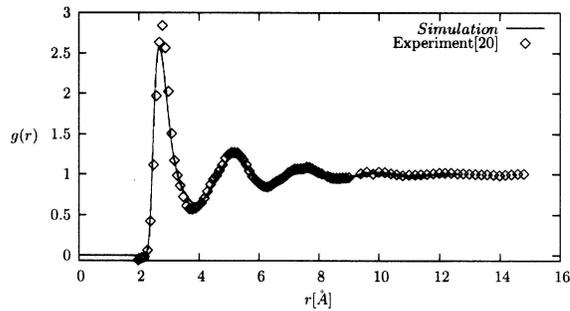


Figure 3. Comparison of the calculated and experimental results of pair distribution function of Al at temperature 943 K and reduced density 0.950.

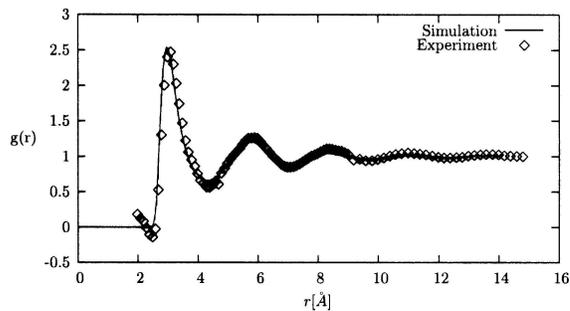


Figure 4. The pair distribution function of Mg as compared with experiment data [20] at temperature 953 K.

and viscosity of liquid Mg decreases with an increase in temperature and a corresponding decrease in density, the positions of the first minimum of $g(r)$ in Mg also increases with decreasing diffusion coefficient and viscosity. The above statement could not be said in the case of liquid Al modelled via the Lennard–Jones potential. This is because it was observed that although, calculations are carried out at close values of densities and temperatures, the relationship between the observed diffusion coefficient, observed viscosity and temperatures or densities are not be linear.

The Lennard–Jones models predict the Stoke–Einstein values very poorly. This is not peculiar to the model as even *ab initio* calculations are only able to predict value of η based on the Stoke–Einstein equation to within 40% accuracy [23]. For Al and Mg the calculated viscosity fall within the observed range [22], as seen in tables 3 and 4. The effect of temperature and density on viscosity could be said to be linear in Mg with the former inversely proportional to the viscosity, while the latter is directly proportional to the viscosity. The linear relationship is not present in the viscosity of Al for the range of investigated temperatures and densities. A reason for this could be ascribed to non-uniform thermal expansion in liquid Al within this range.

For many liquid systems, a dominant factor determining the structure is the packing fraction, hence to include such information on atomic sizes [22] and the ratio of position r_0 to the position of the first peak will shed more light on the arrangements of atoms in the liquid under investigation. It is observed that the ratio r_0/r_{\max} has no effect on packing in the liquid state, as the value is constant at all liquid densities and temperatures. The value obtained from experiment [20] are 0.82 and 0.81 for Al and Mg at 943 and 953 K respectively. From simulation, these are calculated to be ≈ 0.795 and ≈ 0.790 respectively at all temperatures for Al and Mg. From tables 1 and 2, we can see that the packing fraction decreases as temperature increases. This is to be expected, since we have more and more atoms migrating away from the first shell as the average kinetic energy increases. This in turn makes an atom to collide with other atoms more frequently, since an atom in the first shell is likely to possess a higher velocity than the average velocity due to the outward movements of atoms from the first shell. The higher velocity makes it possible to encounter outgoing atoms as well as other atoms present in the shell. And more so, a look at Enskog relation, eq. (6) suggests that for homogeneous simple liquids, as temperature increases, the number of times an atom collides with another atoms increases since $\tau \propto \sqrt{T}$. Figure 1 shows the plots of the pair distribution function of Al at all six investigated temperatures. It is observed that there is no appreciable change in the structure of Al from a temperature of 943 K through 1323 K. This is evident from a perusal of table 1 (packing fraction). There is a total temperature increment of 380 K within the range of temperatures studied in Al, and one expects this value to cause a noticeable effect on the structure of Al. This suggests that liquid Al already has a large heat capacity such that changing its structure requires a large amount of heat energy. If one considers the ratio of the temperature increment to the melting point of Al, we find that this is about 0.162 or 16% and this may not be sufficient enough to cause any noticeable structural change.

Figure 2 is the pair distribution function of Mg at temperatures 953, 1063 and 1153 K. Unlike figure 1, one notices a slight change in the structure of liquid Mg at higher temperature and lower density. There is a slight shift in position of the first peak at $T = 1153$ K and $\rho^* = 0.793$ compared to other lower temperatures and higher densities. The value of $g(r)$ at the first peak is also slightly higher at higher

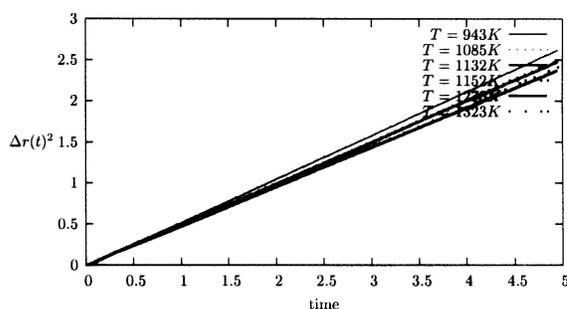


Figure 5. Temperature variation and its effects on the mean square displacement in liquid Al.

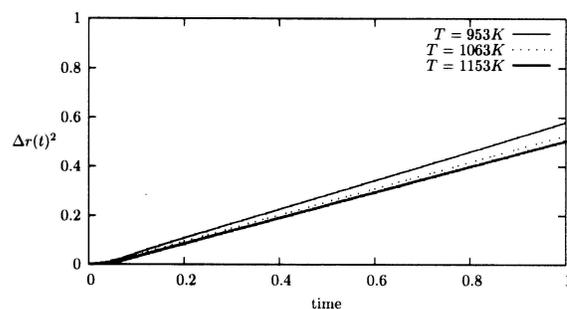


Figure 6. Temperature variation and its effects on the mean square displacement in liquid Mg.

temperatures. In figures 3 and 4, comparisons are made with experimental data on liquid Al and Mg. Apart from few discrepancies at very short distances in the data from experiments containing negative data points, we have very good agreements in both systems with experimental $g(r)$. Figures 5 and 6 show variations of the mean square displacements in the systems studied. These plots corroborate the values of D given in tables 3 and 4. In liquid Mg, there are clear distinctions between the mean square displacements as it is observed that $\Delta r^2(t)$ decreases with increasing temperature. On the other hand, it is possible to distinguish only three clear plots of the mean square displacement in liquid Al, because there are overlap plots of the mean square displacement. The same reasons ascribed in the cases of respective diffusion coefficients can be ascribed to figures 5 and 6.

5. Conclusions

In the absence of a many-body potential function, the interaction between atoms in simple liquids like Al and Mg can be approximated by the Lennard–Jones potential provided the atomic sizes and potential minima are chosen carefully. The interaction model affects the diffusion coefficient and the viscosity and its temperature dependence. The diffusion coefficients are linear with density in the range of investigated temperatures in Mg, but decay as polynomials in liquid Al as temperature increases. From the values of viscosity, one can infer that at higher packing fractions the influence of the softness of the potential core is pronounced. As with other methods of simulation models [23] the Lennard–Jones model predicts value of Stoke–Einstein relation which is not in agreement with the gas limit value. One could then say that, while the static structural parameters, as obtained from the MD simulation, are reasonably correct, the discrepancies found in the dynamical parameters (Stoke–Einstein relation) are clearly the signature of the simplicity of two-body potential approximation, which is quite different from the actual potential in a molten metal. In conclusion, the Lennard–Jones models for liquid Al and liquid Mg systems studied, may not be the best models for Al and Mg. However, they provide quite good information on structural properties in the absence of many-body potential models.

Acknowledgements

The authors acknowledge support from the Abdus Salam ICTP under project PRJ-10. GAA acknowledges computer equipment support from the Deutscher Akademischer Austauschdienst under project No. 131.104401.104. The authors are grateful to the referee for the useful suggestions, comments and constructive criticisms that led to improvement of the manuscript.

References

- [1] R Car and M Parrinello, *Phys. Rev. Lett.* **55**, 2474 (1985)
- [2] J P Hansen and I McDonald, *Theory of simple liquids* (Academic Press, London, 1976)
- [3] D Schiff, *Phys. Rev.* **186**, 151 (1969)
- [4] I J Robertson, V Heine and M C Payne, *Phys. Rev. Lett.* **70**, 1944 (1993)
- [5] F Ercolessi, E Tosatti and M Parrinello, *Phys. Rev. Lett.* **57**, 719 (1986)
- [6] S M Foiles, M I Baskes and M S Daw, *Phys. Rev.* **B33**, 7983 (1986)
- [7] M Körling and J Häglund, *Phys. Rev.* **B45**, 293 (1992)
- [8] V Ozolins and M Körling, *Phys. Rev.* **B48**, 304 (1993)
- [9] B J Alder and T E Wainwright, *J. Chem. Phys.* **27**, 1208 (1957)
- [10] G Kresse and J Hafner, *Phys. Rev.* **B48**, 13115 (1993)
- [11] P E Blöchl and M Parrinello, *Phys. Rev.* **B45**, 9413 (1992)
- [12] G Kresse and J Hafner, *Phys. Rev.* **B49**, 251 (1994)
- [13] A Rahman, *Phys. Rev. Lett.* **32**, 52 (1974)
- [14] J W E Lewis and S W Lovesey, *J Phys.* **C10**, 3221 (1977)
- [15] <http://jas2.eng.buffalo.edu/Research/adesh.txt>
- [16] <http://www.esm.psu.edu/people/students/Graduate/crandow/potentials.htm>
- [17] R W Hockney and J W Eastwood, *Computer simulation using particles* (McGraw-Hill, New York, 1981)
- [18] A Rahman, *Phys. Rev.* **136**, **2A**, A405 (1960)
- [19] S Chapman and T G Cowling, *The mathematical theory of non-uniform gases* (University Press Cambridge, 1939)
- [20] Y Waseda, *The structure of non-crystalline materials, liquids and amorphous solids* (McGraw-Hill International Book Company, 1980)
- [21] D Frenkel and B Smit, *Understanding molecular simulation* (Academic Press, 1996)
- [22] T Iida and R I L Guthrie, *The physical properties of liquid metals* (Clarendon Press, Oxford, 1988)
- [23] D Alfe and M J Gillan, *Phys. Rev. Lett.* **81**, 5161 (1998)