Structure, single-particle and many-particle coefficients of Lennard–Jones liquid Al

G A ADEBAYO$^{1,2,*}$, O AKINLADE$^2$, O A MALOMO$^2$ and L A HUSSAIN$^3$

$^1$The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy
$^2$Department of Physics, University of Agriculture, Abeokuta, Nigeria
$^3$Department of Physics, University of Ibadan, Ibadan, Nigeria

*Corresponding author: E-mail: gadebayo@ictp.trieste.it

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Abstract. We investigate the effects of temperature and density on the single-particle and many-particle coefficients as well as on the structures of homogenous systems in which the particles are assumed to interact via a continuous soft sphere potential in the microcanonical ensemble. The pair distribution function and therefore the structures of the systems studied are affected by temperature close to and above the melting point through migrations of atoms from the first shell in the pair distribution function.

The dynamics of atomic pairs in the short-time regime in liquid aluminium may be said to be governed by the potential of mean force, which depends on the static structure of liquid Al at all investigated temperatures. A polynomial dependence of $D$ on density and temperature was observed in contradiction to Arrhenius law. The shear viscosities of the systems studied are largely nonlinear. It was observed that the soft sphere potential used in our calculations overestimates the Stoke–Einstein relation.

Keywords. Molecular dynamics calculations; viscosity of liquids; structure of liquids; simple liquids and classical ensemble theory.

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1. Introduction

The advent of computer simulation in physics marks the beginning of a new dawn, making computers and very robust algorithms a vital tool not only to physicists, but also to natural scientists and social scientists. The method of molecular dynamics (MD) simulation allows one to obtain information on positions and velocities of atoms in a system obeying Newton’s equation of motion. Analyses of information from the positions and velocities are then used to obtain structural properties, single- and many-particle coefficients. After the second world war, considerable interest arose in methods of computer simulation [1], first to test the capabilities of computer machines of that time and later to provide much insight into several structural, dynamical [2] as well as thermal properties of gases, liquids and solids [3–6]. Numerical computational methods are particularly well-suited to the study of
low-symmetry systems where the complexity of analytical treatments may become overwhelming.

Generally, the predictive power of simulation methods has made both Monte Carlo and molecular dynamics methods to be the standard tool for the study of virtually all fundamental phenomena related to interaction of particles and molecules. Of course, the power of prediction depends on the complexity of the molecular interactions. The key ingredients in computer simulations are the interatomic forces. Although, efficient first principle schemes [7] exist, they require large computing resources and only simple empirical interaction schemes allow studies of large systems and currently, many-body interactions drive up computational costs rapidly and are almost always avoided.

For large systems involving several hundreds or thousands of interacting atoms, force field based method must be used [8]. Methods of molecular dynamics and Monte Carlo simulations which usually treat interactions as pairwise additive, do in many cases describe the structure and particle coefficients of simple homogenous systems exceptionally well [3]. Inclusion of many-body effects into parametrization of pair potential might limit the transferability of force field to a narrow range of thermodynamic conditions.

It is possible to obtain the diffusion coefficient and the shear viscosity in a system by taking statistical averages over time as well as over the particles and taking averages over time on a factor which is proportional to the number of particles. These allow for having minimal statistical error. A standard molecular dynamics calculation with \( N \) number of interacting atoms and the simulation box length \( L \) (in the microcanonical ensemble) is employed in this study to investigate the effect of high temperature and density on the single and collective particles properties as well on the structure of systems modeled through the Lennard–Jones 12-6 potential function.

The calculations are performed using an MD package developed in-house (UNAABMD) that uses the Verlet algorithm to perform the integration of equations of motion for the interacting particles of the system. In this paper, we look at the effect of temperature and density on the single-particle and many-particle coefficients as well as on the structure of Al modeled via Lennard–Jones 12-6 potential function. Systems consisting of 864 particles \((N)\) at various densities and temperatures in periodic boxes of volume \( L^3 = N/\rho \) are studied, where \( \rho \) is the density in reduced unit. The input parameters for the Lennard–Jones model are \( \sigma = 2.62 \ \text{Å} \) and \( (\epsilon/\kappa_B) = 4551.28 \ \text{K} \). In §2, we highlight the method of simulation used in this study. Our results for Al in the liquid form are provided in §3, while in §4 we present our conclusions.

2. Computer simulations

Molecular dynamics simulations of systems, consisting of 864 particles with equal masses taken as unity enclosed in simulation boxes with periodic boundary conditions, were carried out. The interaction potential function usually is of the form
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\[ u(r_{ij}) = 4\epsilon \sum_i \sum_j \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) , \]

(1)

where \( r_{ij} \) is the distance between the interacting atoms \( i \) and \( j \). The sum includes all intermolecular pairs, whereas dispersion and overlap interactions are neglected. The diameter or size of an atom in the system is represented by \( \sigma \) while \( \epsilon \) represents the depth of the potential function. The first term in eq. (1) represents the Coulombic repulsion in the system, while the second term provides attraction at long distances. Simulations were performed at high densities and temperatures above the melting points of the systems. In selecting working conditions, reduced densities and temperatures were chosen to conform with the standard way of selection, i.e. a reduced density, \( \rho^* = \rho \sigma^3 \) and reduced temperature, \( T^* = (K_B T/\epsilon) \).

Initially, particles in the systems were assigned simple cubic configurations, while velocities were set to zero. We have used the standard velocity Verlet algorithm [8] in the MD techniques, interactions are only allowed up to a distance \( r_c = \frac{1}{2}L \), where \( L \) is the length of the simulation box. This is 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 \( \Delta t = 0.004 \) was used to attain thermal equilibrium in each system. Systems were allowed to run for a minimum of 3000 steps to attain equilibration after which data on positions and velocities were collected. Structural calculations are performed through the pair distribution function given by

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

(2)

which is an average over the simulation time steps at equilibrium. The volume of the simulation box with \( N \) particles is \( V \), while \( \Delta N \) represents particles in a shell within the region \( r - \Delta r \) and \( r + \Delta r \), where \( \Delta r \) is the shell thickness, i.e., \( \Delta r \ll r \). In many dense liquids, the relative motion of a pair of atoms is affected by the average force between them. This average force consists of the direct force and the indirect forces intermediate in the \( (N - 2) \) atoms remaining in the liquid. The coordination could be calculated using any of the standard equations, but we have used one method given in [9]:

\[ c_n = 4\pi \int_0^{r_m} \rho(r)r^2g(r)dr, \]

(3)

where \( r_m \) is the first minimum in the \( g(r) \) and since the systems studied are homogeneous systems, this equation then becomes

\[ c_n = 4\pi \rho \int_0^{r_m} r^2g(r)dr. \]

(3')

The average force between the pair of atoms in the system is the gradient of the potential of mean force \( F_W(r) \) and this is given by [10]:

\[ F_W(r) = -K_B T \ln g(r). \]

(4)
We have employed \( g(r) \) obtained from the simulation in the calculation of \( F_W(r) \), \( K_B \) was taken as unity and \( T \) is in reduced unit. The single-particle property investigated in this study is the diffusion coefficient and it is calculated from the mean square displacements of the atoms using the equation

\[
D = \lim_{t \to \infty} \frac{\langle x^2(t) \rangle + \langle y^2(t) \rangle + \langle z^2(t) \rangle}{6t},
\]

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 coordinate axes. It should be noted that these are calculated from the trajectories as a double average over atoms, i.e.,

\[
\langle x^2(t) \rangle = \frac{1}{N \cdot N_T} \sum (x_i(t) - x_i(\tau))^2,
\]

where \( N_T \) represents the number of different time origin \( \tau \) used in the averaging. Analysis of the velocity autocorrelation function also gives the diffusion coefficients \( D \), and from the normalized velocity autocorrelation one is able to obtain the dynamic behaviour of single particles in liquid systems. Both this methods are used in our calculations. The velocity autocorrelation function is given as

\[
c(t) = \langle v(t) \cdot v(0) \rangle.
\]

The many-particle (collective property) coefficient considered in this work is the shear viscosity. This has been calculated using also the Green–Kubo relation and is calculated using

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

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

\[
\sigma_{xy} = \sum_{i=1}^{N} \left( m_i v_{x_{yi}}^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{j>i}^{N-1} r_{ij} f_{ij}(r_{ij}) \right),
\]

\[
f_{ij}(r_{ij}) = -\frac{\partial V(r_{ij})}{\partial r}.
\]

To keep the pressure of the simulated system constant at all times, experimental values of densities \([9]\) were used at corresponding temperatures.

3. Results

In table 1, we tabulate the set of input parameters used in our simulation along with the calculated results on diffusion coefficient and shear viscosity. These parameters are the states of the systems studied. The first three sets of temperatures and densities are taken from experimental data \([9]\), and these data were interpolated to obtain other sets of input parameters such as the temperatures and the
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**Table 1.** Computed values of the diffusion coefficient \(D\), the viscosity \(\eta\) and the main peak values of the pair distribution function of liquid aluminium with coordination from our MD simulation.

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(\rho^*)</th>
<th>Main peak position ((\text{Å}))</th>
<th>(r_m) ((\text{Å}))</th>
<th>(D) ((\text{m}^2\text{s}^{-1}))</th>
<th>Coordination number</th>
<th>(\eta) (mPa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>943</td>
<td>0.950</td>
<td>2.716</td>
<td>3.935</td>
<td>0.112</td>
<td>8.704</td>
<td>3.374</td>
</tr>
<tr>
<td>1023</td>
<td>0.941</td>
<td>2.726</td>
<td>3.949</td>
<td>0.106</td>
<td>8.738</td>
<td>3.016</td>
</tr>
<tr>
<td>1323</td>
<td>0.911</td>
<td>2.754</td>
<td>3.989</td>
<td>0.0995</td>
<td>8.705</td>
<td>1.635</td>
</tr>
<tr>
<td>970</td>
<td>0.947</td>
<td>2.719</td>
<td>3.939</td>
<td>0.110</td>
<td>8.693</td>
<td>2.304</td>
</tr>
<tr>
<td>990</td>
<td>0.945</td>
<td>2.721</td>
<td>3.9418</td>
<td>0.107</td>
<td>8.699</td>
<td>3.963</td>
</tr>
<tr>
<td>1010</td>
<td>0.943</td>
<td>2.723</td>
<td>3.945</td>
<td>0.111</td>
<td>8.704</td>
<td>3.560</td>
</tr>
</tbody>
</table>

**Figure 1.** The potential of mean force in liquid aluminium at temperatures of 943, 970, 990, 1010, 1023 and 1323 K and at respective reduced densities. The potential of mean force (PMF) corresponding to the six representations of the input parameters are displayed in figure 1 for liquid aluminium. For the sets of close parameters, although, the pair distribution functions are similar, the PMF functions differ for a difference of 0.04 ± 0.01 in density values.

The mean square displacements have the same value up to the time steps of 0.05, but beyond this value there is small difference in the values of the mean square displacement, although, at long time steps the values are closer as temperature increases, except at \(T = 1323\) K. The diffusion coefficient obtained from our simulation increases as temperature increases and density decreases except at \(T = 1010\) K and the corresponding reduced density of 0.9427. The values of the shear viscosity at lower temperatures are closer at small time steps, even as the minimum is approached for temperatures 943 K through 1023 K, while at 1323 K the minimum of the shear viscosity is deeper than at other temperatures investigated. However, at long time steps, the value of the viscosity in all the cases approaches zero as can be seen in figure 2. In figure 3, the structures of aluminium at temperatures 943 K and 1023 K are similar with the appearance of the first peak at about the same
value, 2.716 Å and 2.726 Å respectively, while at 1323 K the first peak is at the position of 2.754 Å.

The experimental data of Waseda [9] at 943 K and number density 0.0528 g/cm$^3$ was extracted and a comparison was made with our simulation using similar parameters as given in figure 4. It is expected that the coordination number in the liquid state differs slightly from that of the solid state. Depending on the method used in the determination of this quantity, it is possible to obtain different values for the same structure. In our simulation, when the coordination number of Al in the liquid state was calculated using the position of the first peak a value of $\approx11.44$ was obtained at most of the temperatures, while by integrating eq. (3*) up to the first minimum in $g(r)$, the coordination number determined was $\approx9$.

Our results for the shear viscosity of Lennard–Jones liquid Al is presented in table 1 along with other results. As density increases with corresponding decrease
in temperature, the shear viscosity increases linearly with a change in gradient between $\rho^* = \rho_a$ and $\rho^* = \rho_b$. Afterwards the gradient has a negative value up to $\rho^* = \rho_c$ corresponding to the temperatures at which we can suggest a nonlinear relation in viscosity with density of Lennard–Jones liquid Al. Here $\rho_a$, $\rho_b$ and $\rho_c$ are respectively 0.941, 0.943 and 0.947. It is possible to obtain an approximate estimate of the shear viscosity using its relation with the self-diffusion coefficient $D$ from the Stokes–Einstein relation [11]:

$$D\eta = k_B T / 2\pi d,$$  \hspace{1cm} (11)

where $d$ is the effective atomic size. However, eq. (11) is exact only for macroscopic particles exhibiting Brownian motion, and it is approximate when applied to atoms. Our estimate of eq. (11) differs from the calculated values from our simulation within 50%. This is however within the expected limit, as even the
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\textit{ab initio} calculations of Alfe and Gillan [11] predicts $\eta$ to within 40\% of the Stokes–Einstein value. This was after the diameter $d$ has been adjusted to coincide with the position of the first peak in $g(r)$.

4. Conclusions

The dynamics of atomic pairs in the short-time regime in liquid aluminium may be said to be governed by the potential of the mean force, which depends on the static structures of liquid aluminium. In the long-time regime, the relative motion of an atomic pair in liquid aluminium can be said to be dominated by the direct pair potential between two atoms and is also influenced by the relative motions between the pair and the remaining particles. From the plots of the pair distribution function of liquid aluminium, it is observed that at low density and high temperature, the nearest neighbours of a given atom are repelled from the first shell created by that atom at short-time regime, while beyond this short-time regime, the atoms originally in the first shell diffuse away from that atom. At higher densities and lower temperatures, instead of penetrating through the first shell, the nearest neighbours of a given atom are trapped within the first shell before the shell spreads out in liquid aluminium.

As temperature increases, there is a corresponding increase in the kinetic energy leading to expansion of liquid Al. This obviously gives rise to additional surface (and therefore volume) where the atoms in liquid Al can move. This may be said to account for the increase in coordination number of Al at higher temperatures. In the investigated temperature region, the shear viscosity could be said to be density dependent linearly up to a certain value, with a possible likelihood that the Lennard–Jones Al has a nonlinear relation between viscosity and density between the reduced densities of $\rho^* = 0.941$ and $\rho^* = 0.947$. We would like to point out that the Lennard–Jones potential models the liquid Al system quite well, and the model provides quite good approximation of the structure where many-body potential models are not available.

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References

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