Thermal conductivity of argon: Modeling and comparison with experimental data

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Abstract. The thermal conductivity of argon in solid state phase is modeled by studying the physics property of atom vibrations given by different potentials in crystalline networks at temperature less than 80 K, in the canonical ensemble where volume, mass and temperature are held constant. Molecular dynamics simulations are carried out taking into account the Verlet algorithm and the Green-Kubo formalism. We consider some interatomic interactions as Lennard-Jones, Mie and Kihara potential to obtain results that we compare to experimental data. We show that the present modeling based on the Kihara potential is the best, showing a precision (8.8%), which is not found in recent literature.

Keywords: Thermal conductivity; Interatomic interaction potential; Molecular dynamics.

1. Introduction

In physics, the thermal conductivity, $\lambda$, is the property that allows the heat conduction\[1]\ in materials, which is possible to be assessed via the Fourier law, given by

$$J = -\lambda \nabla T,$$

where $J$ is the heat flux in units $[W/m^2]$, $\nabla T$ is the gradient of the temperature inside of the material in $[K/m]$ and $\lambda$ is the thermal conductivity in units $[W/mK]$. In materials of low conductivity, the heat transfer is less than in materials of high conductivity. In one case, the materials of high conductivity are widely used as heat dissipators. In the contrary case, materials with low conductivity are used as thermal insulators. The thermal conductivity of materials depends on the temperature, and its inverse is the thermal resistivity\[2].

There are proper tools for determining the thermal conductivity for steady and transient states. In general, techniques for the steady states are useful when the temperature is unchanged in time \[2]. At atomic level, there are no simple expressions to phrase the thermal conductivity. Then, there are two perspectives to make this calculation, those are:

(i) Green-Kubo relations, which are employed in the present paper. Although these are analytical, the calculation is carried out by molecular dynamics (MD) for dense fluid and solids\[2].

(ii) Relaxation time approximation. The heat transfer is because of the anharmonicity of the potential in the crystal, which is known as phonon conductivity, studied by the Monte Carlo method\[2].
The MD simulation is for now a well-established method to calculate several transport and thermal properties in fluids [3]. The Lennard-Jones potential has been considered a pivotal model[4], which takes the molecules as hard spheres containing two main characteristics: repulsive at short distance and attractive at intermediate and long distances[5, 6]. There are other models related to potentials of interacting molecules[7]. In this work, we use the following potentials:

\[
\phi_{L-J} (r_{ij}) = 4 \epsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \quad \text{Lennard-Jones, (2)}
\]

\[
\phi_{M14-7} (r_{ij}) = 4 \epsilon \left( \frac{\sigma}{r_{ij}} \right)^{14} - \left( \frac{\sigma}{r_{ij}} \right)^{7} \quad \text{Mie (14-7), (3)}
\]

\[
\phi_{M10-5} (r_{ij}) = 4 \epsilon \left( \frac{\sigma}{r_{ij}} \right)^{10} - \left( \frac{\sigma}{r_{ij}} \right)^{5} \quad \text{Mie (10-5), (4)}
\]

\[
\phi_{K} (r_{ij}) = 4 \epsilon \left( \frac{\sigma(1 + a)}{r_{ij} + a\sigma} \right)^{12} - \left( \frac{\sigma(1 + a)}{r_{ij} + a\sigma} \right)^{6} \quad \text{Kihara (5)}
\]

where \( r_{ij} \) is the distance between the \( i \)-th and the \( j \)-th atom, the parameters L-J, Kihara and Mie are: \( \epsilon/k_B = 119.8[K] \) and \( \sigma = 3.405[\text{Å}] \), and additionally for the Kihara potential we use \( a = 0.01 \). \( k_B \) is the Boltzmann constant. The Kihara potential is defined by Eq.(5). For its parameters we use \( a << 1 \). The Kihara potential is expanded in Taylor series in terms of \( a \) that we show explicitly at first order of approximation, as

\[
\phi_{K} (r_{ij}) = \phi_{L-J} (r_{ij}) - 24 \epsilon \sigma \left[ 2\frac{\sigma^{12}}{r_{ij}^{13}} - \frac{\sigma^{6}}{r_{ij}^{6}} - 2\frac{\sigma^{11}}{r_{ij}^{12}} + \frac{\sigma^{5}}{r_{ij}^{5}} \right] a + O(a^2). \quad (6)
\]

Therefore, the Kihara potential can be written as the L-J potential plus correction terms. Furthermore, the thermal conductivity \( \lambda \) is calculated as [5, 8, 9, 10]:

\[
\lambda = \frac{1}{DVk_B T^2} \int_{0}^{\infty} \langle j(0) j(t) \rangle \ dt, \quad (7)
\]

where \( V \) is the volume, \( T \) is the temperature, the symbol \( \langle ... \rangle \) represents the time average and the factor \( D = 3 \) is related to the dimensions of the systems. The microscopic current is given by[5, 8, 9, 10]:

\[
j(t) = \sum_{i} v_i e_i + \frac{1}{2} \sum_{i,j,i\neq j} r_{ij} [F_{ji} \cdot v_i], \quad (8)
\]

where \( v_i \) is the velocity of the particle \( i \) and \( F_{ij} \) is the force over the particle \( i \) owing he particle \( j \). The energy is estimated by[5, 8, 9, 10].

\[
e_i = \frac{1}{2} \left[ m_i |v_i|^2 + \sum_{j} \phi(r_{ij}) \right], \quad (9)
\]

where \( \phi(r_{ij}) \) stands for different potentials defined by the Eqs.(2)-(5). The Green-Kubo formalism allows us assessing other dynamic properties as the viscosity, electric conductivity, etc., from simulations of atomic systems. Anyway, calculations are made in thermodynamic equilibrium conditions because of results converge for large sizes of systems and large scales.
of time. The size of samples are considered as 108, 256, 500, 864, 1372, 2048, 2916 and 4000 particles, with computation time as $10^6$, with temperatures less than 80 [K].

There are reported previous calculations through MD simulation with precision greater than 10% compared with experimental data [11, 12, 13]. Some variations of the L-J potential are proposed in the literature, for instance L-J potential of Kihara-type [13] and Mie (14,7) potential[7, 14].

The main aim in the current contribution is to compare the thermal conductivity of argon obtained from intermolecular interaction proposed in Eqs.(2)-(5) to experimental data[15, 16]. We expect to perform MD simulations in the NVT ensemble to find out which model gives the best precision related to referred experimental data.

2. The model
At the beginning of simulation, atoms in fluids are settled on face-centered cubic (FCC) [1, 17]. The argon at environment temperature is at gaseous state phase.

2.1. Simulation
The MD simulation is a method which solves numerically the equations of motion for a system of $N$ interacting particles and derive dynamical, thermodynamical and structural properties of the system[17, 18].

2.2. Initial conditions
The system evolves keeping the particle number ($N$), the volume ($V$) and the average temperature ($T$) fixed. This outlook is known as canonical ensemble or NVT ensemble. According to statistical mechanics we know that the translation velocities of atoms in a classical system are distributed by the Maxwell-Boltzmann distribution. Then, if the temperature of the system $T$, the probability of velocity of an atom is between $v$ and $(v + dv)$ is:

$$f(v)dv = \sqrt{\frac{m_i}{2\pi k_B T}} e^{-\frac{m_i v^2}{2k_B T}} dv.$$  \hspace{1cm} (10)

The initial values of velocities are related to a distributions given by

$$T = \frac{2}{N_{df} k_B} \langle K \rangle,$$  \hspace{1cm} (11)

where $N_{df}$ corresponds to the freedom degree of the system and $\langle K \rangle$ is the mean kinetic energy. The following expression can be instantaneously used

$$T(t) = \frac{2}{N_{df} k_B} K(t).$$  \hspace{1cm} (12)

This equation allows us relating the instantaneous temperature to velocities after starting the simulation[19].

2.3. Periodic boundary conditions
The simulation is frequently carried out using a finite and small number $N$ of particles because of the time spent to obtain results increases with $N^2$. In the current contribution we consider a sample of $N$ particles where $108 \leq N \leq 8000$, which is found in a central cube. To apply periodic boundary conditions means to make infinite replicas of the original cube. Image particles move in the same way as the original particle does. If a particle goes out of the original cube, other particle comes in by the opposite size. Thus, the total number of particles inside the original cube and its replicas remains constant[20].

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Figure 1. Thermal conductivity, $\lambda$, as a function of the size of systems, $N$, is depicted for L-J, Mie (14-7), Mie (10-5) and Kihara potential.

Figure 2. Thermal conductivity, $\lambda$, as a function of the cutoff, $r_c$, is depicted for potentials as L-J, Mie (14-7), Mie(10,5) and Kihara.

2.4. Force calculation
If we consider a system of $N$ interacting particles in a volume $V$. The internal energy of the system is given by

$$E = K + U,$$

where $K$ is the kinetic energy; $U = U(r_1, r_2, r_3, ..., r_N)$ is the potential energy of interacting particles and $r_i(t) = (x_i(t), y_i(t), z_i(t))$ is the position vector of the $i$-th particle. In the NVT ensemble, the temperature $T$ remains around its expected average and the evolution of the system is governed by a conservative outlook given by equations of motion

$$F_i = -\nabla r_i U,$$

where $F_i$ is the net force over the $i$-th particle due to other, which is derived from the potential energy $U$ [18].

Other relevant aspect is to take into account the reduced units in the simulation, which are: $r \rightarrow r \sigma$, $E \rightarrow E \epsilon$, $t \rightarrow t/\sigma \left(\frac{m}{\epsilon}\right)^{\frac{1}{2}}$, $T \rightarrow T \left(\frac{\sigma^2}{\epsilon}\right)$, $P \rightarrow P \left(\frac{\sigma^2}{\epsilon}\right)$, $v \rightarrow v \sqrt{\frac{\epsilon}{m}}$ and $F \rightarrow F \left(\frac{\sigma}{\epsilon}\right)$; where $r$ is the position, $E$ is the energy, $m$ is the mass, $T$ is the temperature, $P$ is the pressure, $v$ is the velocity and $F$ is the force. When $r_{ij} < r_{\text{min}}$, the interaction is repulsive and when $r_{ij} > r_{\text{min}}$ the potential is attractive. The potential Mie (14-7) has a range shorter than Mie (10-5) and this latter larger than L-J potential. The Kihara potential compared to L-J potential has additional terms analytically given by Eq.(6). Therefore, the interaction force between $i$-th and $j$-th atoms is defined by $F = -\nabla \phi$.

2.5. Thermal conductivity
The thermal conductivity, $\lambda$, graphically corresponds to the area under the curve of the autocorrelation heat current as a function of the time, where its discrete form is given by[9, 13]

$$\lambda = \frac{\Delta t}{3V k_B T^2} \sum_{m=1}^{M} \frac{1}{N - m} \sum_{n=1}^{N-m} \mathbf{j}(n) \cdot \mathbf{j}(m + n).$$

(15)
2.6. Other parameters
We carry out simulations of samples using equations defined before, with times $10^5$ and $10^6$ in simulation units. The useful temperatures are $T = 20, 30, 40, 50$ and $60$ [K]. We use in each calculation the defined potential of interaction as Lennard-Jones, Mie (14-7), Mie(10-5) and Kihara defined in Eqs.(2)-(5) We use the NVT ensemble taking samples with $N = 108, 256, 500, 864$ and $1372$. Our test was made with reduced density $\rho^\ast = 1\cdot043$ and cutoff given by $2\sigma, 2.3\sigma, 2.5\sigma, 2.8\sigma$ and $3\sigma$ at temperature $T =50$ [K] for each defined potential Results are depicted in Figure 1 and Figure 2 to show that the dependence on cutoff $r_c$ and the size of samples $N$ are practically negligible. Thus, we choose the cutoff as $r_c = 2.5\sigma$ and $N = 500$.

3. Discussion of results and concluding remarks
The values of thermal conductivity are calculated by MD simulation using the Green-Kubo formula and the Verlet algorithm for each potential of interaction. The experimental data were measured by D.K.Christen and G.L.Pollack [15] and I.N.Krupskii and Manzhelii [16].

In Figure 3, the thermal conductivity as a function of temperature is depicted for L-J, Mie(14-7), Mie(10,5) and Kihara potentials. In Figure 4, the relative difference of the thermal conductivity related to experimental data, $\lambda/\lambda_{exp} - 1$, as a function of temperature, $T$, is shown for L-J, Mie(14-7), Mie(10,5) and Kihara potentials. The correlation and the precision

| Potential   | Correlation | Precision |
|-------------|-------------|-----------|
| Kihara      | 0.967 Kr    | 8.8%      |
| Mie (14,7)  | 0.894 Kr    | 22%       |
| Mie (10,5)  | 0.939 Kr    | 16.7%     |
| L - J       | 0.962 Kr    | 15.9%     |
| Kihara      | 0.983 Ch    | 28.7%     |
| Mie (14,7)  | 0.999 Ch    | 46.7%     |
| Mie (10,5)  | 0.985 Ch    | 44.4%     |
| L - J       | 0.999 Ch    | 43.7%     |

Table 1. Correlation and precision among experimental data and calculated values.
of the theoretical values related to experimental data are presented in the Table 1, where the correlations related to D.K.Christen G.L.Pollack is denoted as \( \text{Ch} \), and related to I.N.Krupskii and Manzhelii is denoted as \( \text{Kr} \).

We notice that the Kihara potential in the way defined in Eq.(5) is the model that presents the best results based on the Figure 4 and the Table 1. Kihara presents the lowest relative difference with the data and the best values of precision related to range measured by each authors. We think other properties can be calculated by Kihara potential in the future for the argon and other elements in its solid phase as krypton and xenon.

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