Prediction of the thermal conductivity of gas mixtures using direct simulation monte carlo method

Mohamed M. Elafify [a], Khalil M. Elawadly [b] and Sherif G. Elsharkawy [c]

[a]*Nuclear Eng., and* [b] *Mathematics & Eng. physics Depts., Faculty of Eng., Alexandria University, Alexandria Egypt*
[c] *College of Eng. and Technology, Arab Academy for Science and Technology (AAST), Alexandria, Egypt*

The thermal conductivity of gas mixture filling the gap between two parallel plates was obtained and analyzed using Direct Simulation Monte Carlo technique (DSMC). The thermal conductivity of the gas mixture is not a simple linear relation between the conductivities of gas species in the mixture. The DSMC method provides the right technique for simulating molecules to determine the thermal conductivity of the mixture. The molecules are considered as hard sphere ones while the gas gap boundaries are diffusive surfaces. As a verification to the developed code two cases of heat transfer in one dimension between two parallel plates subjected to temperature differences are considered. Two sets of values of temperatures had been used. The first set considers the hot and cold plate temperatures at 325.7 K and 245.7 K, respectively. This set is used to examine the efficiency and credibility of the DSMC method when used for a gas mixture and to assure that the results show the expected temperature and pressure profiles similar to those obtained in the case of single gas molecules. The second set uses temperatures of 306 K and 300 K to evaluate the thermal conductivity at the average temperature value of 303 K to compare with available experimental results. The molar fractions with position had been checked to make sure that the DSMC simulates the collisions and motion of different gas molecules in the right way. The thermal conductivities are calculated in details for Neon / Argon gas mixtures with different molar concentrations and the results are presented together with experimental results for the same mixture. There is a good agreement between the code results and the experimental ones. The DSMC technique is a well-established method to represent and calculate the macroscopic properties of a gas mixture especially when the gas is in the transition region between continuum and free molecular regimes.

الحسابات الدقيقة لمعامل التوصيل الحراري لخليط من الغازات تعتبر من التطبيقات التى يصعب حلها بالطريق التحليلية رغم أهمية معرفة معاملات التوصيل التى تعتبر من البيانات الأساسية المطلوبة لاتمام الحسابات فى كثير من التطبيقات الهندسية. بمراجعة الأبحاث المنشورة نجد أن القليل منهم هم الذين تعرضوا لهذه النقطة رياضيا. إلا أنها درست عمليا فى عدد من المراجع. فى هذا البحث تم حساب وتحليل التوصيل الحراري لخليط من الغازات يملأ الفراغ بين لوحين متوازيين باستخدام طريقة المحاكاة المباشرة مونت كارلو عند وجود فرق فى درجة الحرارة بين اللوحين. تم اعتبار الجزيئات ككور صلبة بينما اعتبرت الحدود الفاصلة للغاز كأسطح مشتتة. للتأكد من سلامة البرنامج الذى تم اعداده درست حالتان لخليط الغاز. فى الحالة الأولى كانت درجة حرارة اللوح الساخن والبارد هما على الترتيب ٣٢٥,٧، ٢٤٥,٧ درجة كلفن وهذه الحالة تم استخدامها لحساب توزيعات درجة الحرارة والضغط المتوقعة والمشابهة لحالة جزيئات الغاز النقي والتي تم دراستها في بحث سابق. الحالة الثانية هى لدرجات حرارة ٣٠٦ درجة كلفن للوح الساخن و ٣٠٠ درجة كلفن للوح البارد وهذه الحالة استخدمت لمقارنة نتائج الكود المعد مع النتائج العملية لباحث أخر. تم التأكد من سلامة الكود ودقته أيضا من حساب نسب التوزيع للجزيئات مع الموضع. أظهرت النتائج أن معامل التوصيل الحراري لخليط من الغازات لا يرتبط مع معاملات التوصيل لغازات الخليط فى حالتها النقية بعلاقة خطية بسيطة. خلاصة البحث تفيد أن طريقة المحاكاة المباشرة مونت كارلو هي طريقة مميزة لحساب وتمثيل الخواص الماكروسكوبية لخليط من الغازات خاصة عندما يكون الغاز في المنطقة الانتقالية فيما بين المنطقة الاستمرارية ومنطقة الجزيئات الحرة.

1. Introduction

A precise values of the thermal conductivity of gas mixtures is valuable in many engineering applications. In gas gap of a nuclear reactor fuel element, helium and gaseous fission products form an example of such applications. Another application is in

Gas Cooled Reactors (GCR's), where gas properties are important for calculation of temperature profiles in fuel. Also, in many welding and contact applications the thermal conductivity of the gas is needed to calculate the contact heat transfer coefficient precisely. However, owing to experimental difficulties, few numerical data are available. A precise formula governing the composition dependence of the thermal conductivity of gas mixtures in terms of values of its pure components is hardly available [1]. A number of expressions [1] have been proposed which have met varying degrees of success. It is logical that, the thermal conductivity of these mixtures should be first fully understood, at a molecular level, before trying to expand calculations to more complex situations. This is the aim of this paper.

A theory of thermal conductivity of gases using dense hard sphere model was worked out by Thorne [2], who extended the Enskog theory to dense hard sphere mixtures. Dipippo et al. [3] presented a method, based on the modified theory presented by Thorne, allows the computation of thermal conductivity of binary mixtures of mono-atomic gases. The method uses measurements of the thermal conductivity for the pure components up to the same density as for the mixtures together with the zero-density thermal conductivity at one composition for a given gas. Anathony et al. [4] measured the thermal conductivities of gaseous mixtures of helium with hydrogen or deuterium at 77.6 and 283.2 K. The results they obtained are shown to be accurately predictable on the basis of the Hirschfelder-Eucken eq. [5] using a potential function for the interaction between a helium atom and a hydrogen molecule calculated quantum mechanically by Tsapline and Kutzelnigg [6].

2. Direct simulation monte carlo technique for gas mixtures

The Direct Simulation Monte Carlo method had been used by Elafify et al. [7] to calculate the thermal conductivity of pure noble gases. Their work has showed a good agreement with the 8-moment method. Expanding the technique to gas mixture consisting of a total of s separate species (p, q,...etc), the Boltz-

mann equation becomes a set of simultaneous equations. The Boltzmann equation for species p of the mixture can be written in the form [8]:

$$\frac{\partial}{\partial t}(n_p\, f_p) + \mathbf{c}_p \cdot \frac{\partial}{\partial \mathbf{r}}(n_p\, f_p) = \sum_{q=1}^{s} \int_{-\infty}^{+\infty} \int_{0}^{4\pi} n_p$$
$$n_q\left(f_p^*\, f_{1q}^* - f_p\, f_{1q}\right) c_{rpq}\; \sigma_{pq}\; d\Omega\; dc_{1q}. \qquad (1)$$

Where:

$\mathbf{c_p}$, $\mathbf{c_{1q}}$ are the velocity vectors of the colliding partners,

c_{rpq} is the relative speed between particles of species p and q, respectively=$|\mathbf{c_p}$- $\mathbf{c_{1q}}|$,

f_p, f_{1q} are the distribution functions of colliding particles before collision,

f_p^*, f_{1q}^* are the distribution functions of colliding particles after collision,

n_p is the molecular density for species p,

n_q is the molecular density for species q,

σ_{pq} is the collision cross section of the molecules of the two species p and q,

Ω is the solid angle,

t is the time, and

$\mathbf{r}$ is the position vector.

The exact solution of such an integro-differential equation is complicated. Another technique of attacking such a problem is the use of Monte Carlo method. The Direct Simulation Monte Carlo method (DSMC) is a simulation method applied to simulate the real gas flow through the field of propagation.

Throughout this work the DSMC method is used to calculate the thermal conductivity for gas mixture. The essential approximation introduced in the solution using the DSMC is the uncoupling of the molecular motion and the intermolecular collisions over a small time interval or step Δt_m. In the simulation, all molecules are moved (including the computation of the resulting boundary interactions) over a distance appropriate to this time step. This is followed by the calculation of a representative set of intermolecular collisions for sum of time intervals Δt_c's that are appropriate for the time interval of the motion Δt_m. The time interval of any collision should satisfy the collision frequency appropriate for each species in the mixture. Using the expression given in [8] for Δt_c:

$$\Delta t_c = \frac{1}{N_p} \frac{1}{\sigma_{pq} \, n_q \, c_{rpq}} + \frac{1}{N_q} \cdot \frac{1}{\sigma_{pq} \, n_p \, c_{rpq}}, \quad (2)$$

here, N_p is the simulated number density of species p and N_q is the simulated number density of species q.

The mean collision rate for a species p molecule with species q molecule is given in [8] as:

$$v_{pq} = 2\sqrt{\pi} \, d_{eff}^2 \, n_q \left\{ \frac{2KT(m_p + m_q)}{m_p m_q} \right\}^{\frac{1}{2}}, \quad (3)$$

where d_{eff} is the effective collision diameter of the two molecules as given in [8] by:

$$d_{eff} = \frac{d_p + d_q}{2.0}. \quad (4)$$

Also, the mean collision rate for species p molecules is given by:

$$v_p = \sum_{q=1}^{s} v_{pq}, \quad (5)$$

and the mean collision rate per molecule for the mixture is given by:

$$v = \sum_{p=1}^{s} \left\{ \left(\frac{n_p}{n} \right) v_p \right\}. \quad (6)$$

The equilibrium mean free path for species p molecules is given by:

$$\lambda_0 = \sum_{p=1}^{s} \left(\frac{n_p}{n} \left[\sum_{q=1}^{s} \left\{ \pi d^2 n_q \left(1 + \frac{m_p}{m_q} \right)^{\frac{1}{2}} \right\} \right]^{-1} \right). \quad (7)$$

The time step should be small in comparison with the mean collision time.

The hard sphere model is used to represent collision cross-section between molecules in the mixture. The collision partners are chosen according to the collision probability of molecules. The collision prob-

ability of molecules increases with increasing the quantity $\dfrac{\sigma_{pq} c_{rpq}}{\left(\sigma_{pq} c_r \right)_{max}}$.

The hard sphere cross-section is given by the following relation [8]:

$$\sigma_{pq} = \pi \, d_{eff}^2. \quad (8)$$

In the simulation, an acceptance-rejection technique has been adopted to choose the collision partners based on $\sigma_{pq} \, c_{rpq}$. In the mean time, an acceptance–rejection technique based on position in the cell is adopted to choose partners for collisions. Despite of the fact that collisions do not depend on the position of molecules inside the cell, the probability of collision increases as the partners are closer to each other. The cell network is required only in physical space. This space network is used to facilitate the choice of the collision partners and for sampling of the macroscopic flow properties. The collisions are always treated as three-dimensional phenomena. The procedures for the establishment of the correct collision rate are based on the cells. After the collision takes place for the time interval Δt_c. The pre-collision velocity components are replaced with the post-collision values. For gas mixtures, it is favorable to consider the molecular masses of different species; this is because the collision frequency of heavy-heavy molecules collisions would be small compared with that for light-light ones. Moreover, the cross collisions between light and heavy molecules would have little effect on the heavy gas. These will set the value of $\left(\sigma_{pq} \, c_r \right)_{max}$, the acceptance rate for the heavy molecules will be low and the overall selection will be insufficient. So, for a collision between species p and q the acceptance condition is given by [8]:

$$\frac{\sigma_{pq} c_r}{\left(\sigma_{pq} c_r \right)_{max}}.$$

When reaching the steady state heat flow, the properties in each cell are sampled and the output macroscopic properties like

temperature, pressure, heat flux and thermal conductivity are calculated by the expressions:

$$T = \frac{2}{3\,k\,N_{c\,final}} \sum_{i=1}^{N_{c\,final}} \frac{1}{2}\,m\,c_i^2 \,,$$

$$P = \frac{n_{act}}{N_{c\,initial}} \times N_{c\,final} \times k\,T \,,$$

$$q_x = \frac{n_{act}}{N_{cinitial}} \sum_{i=1}^{N_{c\,final}} \frac{1}{2}\,m\,c_i^2\,c_{xi}\,\vec{a}_x \,,$$

where: k is the Boltzmann constant, $N_{c\,final}$ is the number of simulated molecules in each cell, m is the molecular mass n_{act} is the actual number density of molecules and $\boldsymbol{a}_x$ is a unit vector in the x-direction and c_x is the velocity component in the x-direction

3. Code-verification

A computer code has been developed to perform the DSMC technique for the determination of thermal conductivity of mono-atomic gas mixtures. This code is applicable to any mixture of such type of gases with any partial pressures.

For the sake of comparison with previous experimental results [4], the following test problems have been set.

Two species of molecules of inert gases (Neon and Argon) are used to simulate the real gas mixture that is filling the field between two parallel plates. The position, velocity components, molecular masses, molecular diameters and initial temperatures for a gas mixture species that are uniformly distributed in physical space are stored in the computer memory.

At start up of the Monte Carlo simulation all molecules are picked out from the maxwellian distribution at the temperature of the cold plate. Different number density ratios for the chosen species are used as have been done by Kisten et al. [9]. The ratio of each species is taken as the ratio of the partial pressure for each one according to the relation:

$$p_i = n_i kT \tag{9}$$

Where:

p_i is the partial pressure.
n_i is the number density of molecules of species i.
K is the Boltzmann constant.
T is the Absolute temperature.

Appropriate precautions are taken to ensure that the used data would satisfy the dilute gas conditions. These precautions consider the relation between the characteristic length L between the two parallel plates, the mean free path between molecules and the value of the mean molecular spacing between molecules. The dilute gas requires that the Knudsen number Kn should be small compared with unity. The corresponding value of the characteristic length L is at least ten times as large as the side of a cubic element containing 1000 molecules. The number of molecules per species in each cell should not be lower than 10 in order that the fluctuations are minimum. The number of molecules in each cell is taken as 50 molecules per cell. The simulated molecules are arranged in one-dimensional array in the field between the two plates. At this moment, the molecular motion is initiated for all molecules and their mean free paths are calculated for each type of the two species. Minimum mean free path is chosen and applied to calculate the total number of cells through out the characteristic length L. All molecules are moved through a distance appropriate to a time interval Δt_m. After that, all molecules are enforced to experience the principle of acceptance-rejection techniques based on both $\sigma_{pq}c_r$ and position to choose the most probable molecules that are best neighbors to undergo a collision. Under this principle, all molecules of the two species are collided with one another regardless of their types. The time counter increases by time increments Δt_c according to the collision partners till the cumulated time of collisions finally reaches a value appropriate to the time of motion Δt_m. When the time of simulation Δt_s reaches a value at which the medium between the two parallel plates reaches the equilibrium state, the steady flow condition is achieved. Then, all macroscopic properties such as temperature, pressure and density profile are determined by the code. Finally, the heat flux and thermal

conductivity of the gas mixtures are calculated.

In the calculations, two sets of values of temperatures have been assumed. The first set considers the hot and cold plate temperatures at 325.7 K and 245.7 K respectively. This set is used to examine the efficiency and credibility of the DSMC method and to assure that the results show the expected temperature and pressure profiles when only single gas molecules are considered. The second set uses temperatures of 306 K and 300 K to evaluate the thermal conductivity at the average temperature of 303 K. This value has been picked up to represent the case of the experimental work given by Dipippo et al. [4].

For evaluating the statistical errors in the Monte Carlo results, batches of runs with different sets of random numbers are performed. At least four batches are executed for each composition with 50 molecules per cell in each run. The total number of simulated molecules in the field is around 20,000 molecules in each run. More batches are calculated in cases of compositions of low partial pressure of either of the two components. As expected, it is found that, when partial pressure of any of the components is low, the error in calculations is higher if the same number of batches were used. Up to 8 batches are considered in these cases. This is interpreted by the low number of simulating molecules of such type when the total number of molecules per cell is fixed.

4. Results and Discussion

Figs. 1-a to 1-c show the temperature, density and pressure profiles for the test problem with the first set of temperature values (245.7 K & 325.7 K). The values are normalized to conditions at cold plate temperature they are similar to the figures obtained for a single gas [1]. These figures show that the developed code has succeeded to simulate the case of a gas mixture.

As a second check for evaluating thermal conductivity at 303 K, the second set of data for temperatures 300 K and 306 K have been used. It is obvious that, the gradients are not clear in fig. 2-a to 2-c since the difference
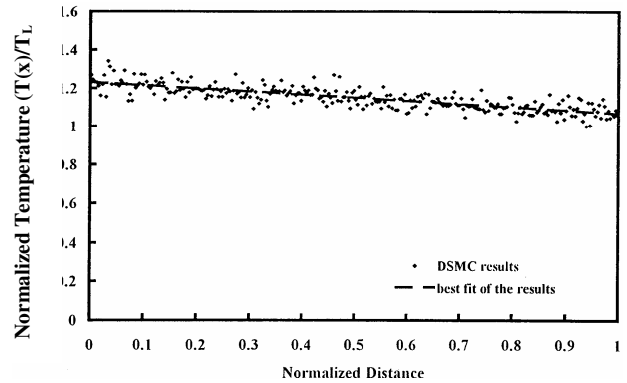

Fig. 1-a. Normalized temperature profile for a gas mixture combination of 0.61 Neon & 0.39 argon fractions at pressure 1.01 bar and temperatures 325.7 K & 245.7 k.
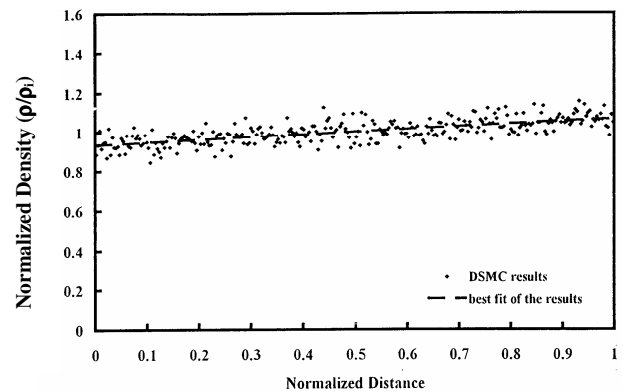

Fig. 1-b. Normalized density profile for gas mixture combination of 0.61 Neon & 0.39 argon mole fractions at pressure 1.01 bar and temperature 325.7 K & 245.7 K.
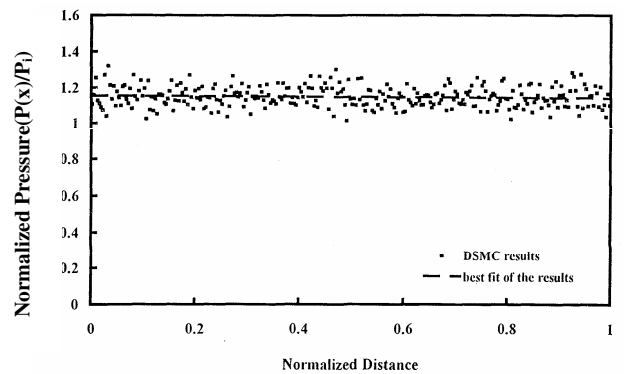

Fig. 1-c. Normalized pressure profile for a gas mixture combination of 0.61 Neon & 0.39 argon mole fractions at pressure 1.01 bar and temperature 325.7 K & 245.7 K.

in temperature between hot and cold plates is low. Similar behavior for the temperature, density and pressure distribution are found when varying the Neon mole fraction in the mixture.

As a third verification for the developed code, the relative number of the simulated molecules for both Neon and Argon gas in each cell are counted for all the considered examples. The expected partial pressures are achieved in each case with the pre-assumed values. As an example of these results the case of a mixture of Noen and Argon is shown in fig. 3. As can be noted, the mole fraction fluctuates around its average value in each cell. The curve shows that, there is no accumulation of any of the two species of the gas mixture at any position, which assures the uniform distribution of the mixture and right representation of the collision and motion of simulated molecules. In spite of the variation in number density in each cell, the molar fractions are invariant.

Fig. 2-c. Normalized pressure profile for a gas mixture combination of 0.205 Neon & 0.795 argon mole fractions at pressure bar and temperature 300 K & 306 K.

5. Heat flux and thermal conductivity

Fig. 4 shows sample of the outputs of the heat flux against time. The heat flux value fluctuates around an average value for different composition of the gas mixtures, which means that, the steady state equilibrium has been achieved. A time average is used to determine the average value of heat flux within the gas.

As an example to the numerical results that can be obtained using the developed code, the case of a binary mixture of Neon / Argon is studied in details. The concentration of Neon in the mixture varies from 0.1 to 0.9. The results are shown in fig. 5.

The figure shows the thermal conductivity of gas mixture at different values of compositions compared with the experimental data taken from Garrabos (in ref. [4]). The curve uses a plot of best-fit polynomial to show the calculated results. Error bars are used to represent the error percentage in these when the DSMC method is used. It is obvious from the figure that the DSMC results are in good agreement with the experimental data. Despite of the high error associated with some of the considered cases, the DSMC method is the most reliable technique when approaching the free molecules level where Knudsen number greater than 0.1 since it has no approximations and it doesn't assume the continuum model.
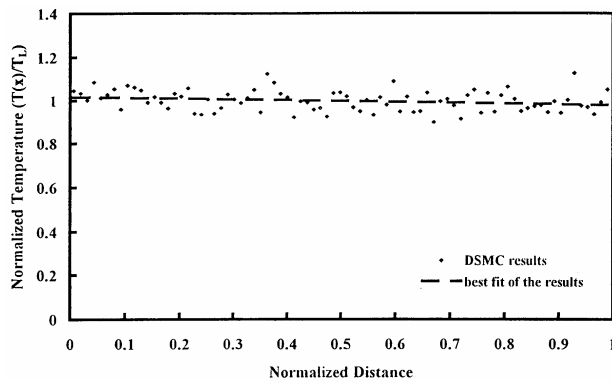

Fig. 2-a. Normalized temperature profile for a gas mixture combination of 0.205 Neon & 0.795 argon mole fractions and temperature 300 K & 306 K.
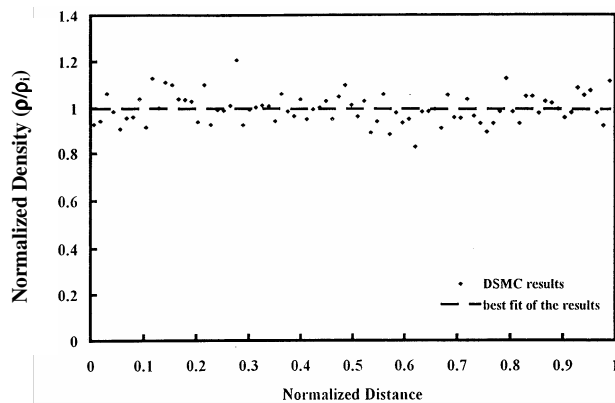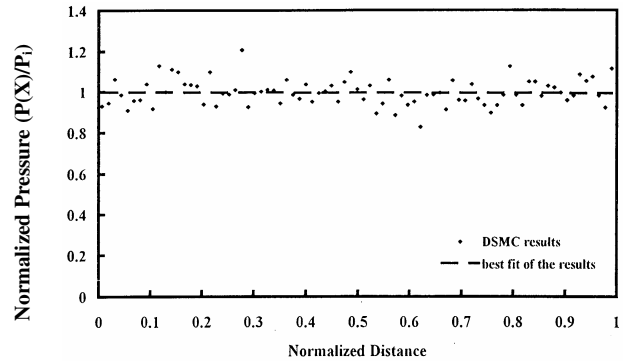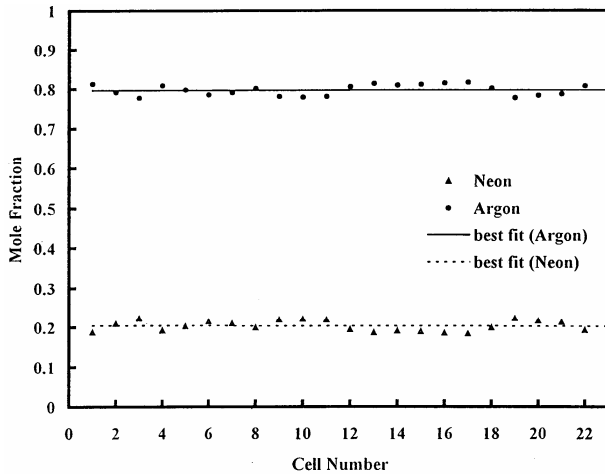

Fig. 2-b. Normalized density profile for a gas mixture combination of 0.205 Neon & 0.795 argon mole fractions at pressure 1.01 bar and temperature 300 K & 306 K.

Fig. 3. The disribution of the molar fractions for the gas mixture ratios of neon (0.205) & argon (0.795) along the normalized distance between the two parallel plates at steady state.
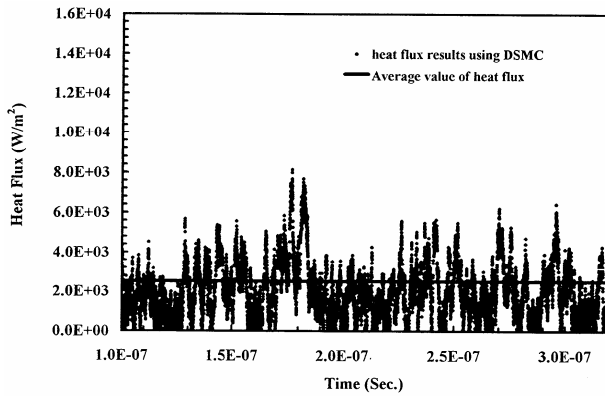

Fig. 4. Heat flux pattern between the two parallel plates having temperature 300 K and 306 K Neon concentation of 0.55.
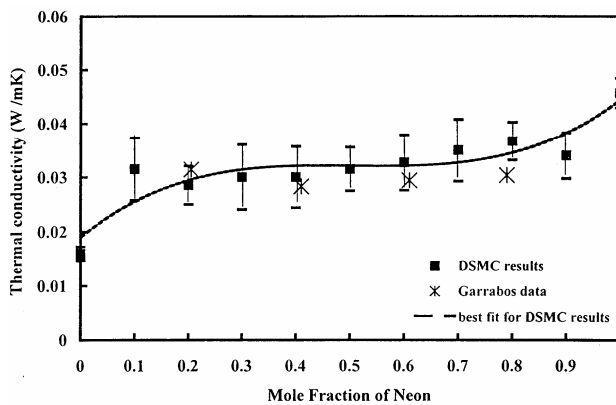

Fig. 5. Comparison between the thrmal conductivity results obtained from DSMC method & the experimental data obtained from differenet combination of gas mixtures neon & argon.

6. Conclusions

The thermal conductivity of gas mixture consisting of two different species of mono-atomic gas at 1.01 bar and 303 K have been examined using DSMC method. The values of thermal conductivity of the mixture has been determined at different mole fractions and compared with experimental results. Different batches of runs have been executed to calculate the statistical error in the determined values. The error was less than 15% in all cases. It has been found that the thermal conductivity of the gas mixture is not a simple linear relation depending on the thermal conductivities and molar fractions of the species. The error bars show that the statistical error increases as one of the species concentration is much lower than the other. For pure gases this error is at minimum since all simulating molecules are of the same type. The results are consistent and the relative differences between the experimental and Monte Carlo results are within the statistical fluctuations of the method arising due to low number of simulating molecules than real ones. The developed model is a well-established method for representing and calculating the macroscopic properties of a gas mixture especially when the gas is in the transition region between continuum and free molecular regimes. It can be also concluded that, the DSMC method is unique in representing the gas molecules for various Knudsen numbers.

References

[1] R. Bird, W. Steward E. and Lightfoot Transport Phenomena, John Wiley & Sons., New York (1960).

[2] W. McElhannon, and Mclaughlin, "The Thermal Conductivity of Simple Dense Fluid Mixtures", Proceedings of the 14th International Conference on Thermal Conductivity, Storrs, Connecticut, U.S.A. pp. 345-352 (1975).

[3] R. Dipippo, J.R. Dorfman, J. Kestin, H.E. Khalifa, and E.A. Mason, "A Theory for the Composition Dependence of the Thermal Conductivity of Dense Binary Mixtures of monoatomic gases", proceedings of the

14th International conference on thermal conductivity, Storrs, Connecticut, U.S.A. pp. 326-329 (1975).

[4] A. Anathony, Clifford, L. Colling, E. Dickinson and P. Gary, "Thermal Conductivities of Gaseous Mixtures of Helium With the Hydrogen Isotopes at 77.6 and 283.2 K", Proceedings of the 14th International conference on thermal conductivity, Storrs, Connecticut, U.S.A., pp. 337-344 (1975).

[5] J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, The Molar Theory of Gases and Liquids, John Wiley & Sons, New York (1964).

[6] B. Tsapline and Kutzelnigg, Chem. Phys. Lett., Vol. 23, p. 173 (1973).

[7] M. Elafify, K. Elawadly, S. Elsharkawy, and M. Bassiouny, "Heat Transfer in Nobel Gases Using Direct Simulation Monte Carlo technique (DSMC)", Pakistan Journal of Applied Sciences, Vol. 2 (12), pp. 1050-1056 (2002).

[8] G.A. Bird, "Molecular Gas Dynamics and the direct Simulation of Gas Flows," Oxford university press, (1994).

[9] J. Kestin, S.T. Ro, and W.A. Wakeham, "Viscosity of the Noble Gases in the Temperature Range 25-700 ^{o}C," J. Chem. phys., Vol. 56 (8), p. 4119 (1972).