

Evaluating the Second Virial Coefficients and Thermal Conductivity of Polar Fluids: A Computational Study Using Canonical Ensemble Techniques

Dr. Rajesh Kumar¹, Dr. Rajendra Kumar²

¹Associate Professor, Department of Physics, Government Degree College, Nanauta, Saharanpur, U.P.

²Associate Professor, Department of Physics, S.D.PG. College, Muzaffarnagar

Abstract- Understanding the thermophysical properties of polar fluids is essential for various scientific and industrial applications. This study presents a computational analysis of the second virial coefficients and thermal conductivity of polar fluids using canonical ensemble techniques. By taking the canonical average of the Rowlinson potential and introducing it into the forces parameters of the Leonard-Jones potential, it is a useful suitable effective potential that is temperature dependant. The temperature-dependent parameters that we derive are utilized to compute the effective potential at various temperatures. We created a temperature-independent graph using the Lennard-Jones potential. The experimental and canonical effective potential values of water vapour at various temperatures. There is an excellent match between the experimental value of water vapour and the temperature-dependent CAP value of the second virial coefficients and thermal conductivity.

Index Terms— Canonical Average Effective Potential, Lennard-Jones Potential, Rowlinson Potential, Second Virial Coefficients, Thermal Conductivity, Collision Integral.

I. INTRODUCTION

The study of intermolecular interactions in fluids is pivotal for understanding and predicting their thermodynamic and transport properties. Among these properties, the second virial coefficient and thermal conductivity are of particular significance, especially for polar fluids, which exhibit complex behaviors due to their strong dipole-dipole interactions^{1,2}. The second virial coefficient provides critical insights into the non-ideal behavior of gases, offering a quantitative measure of intermolecular forces that deviate from ideal gas laws at low to moderate densities. Thermal conductivity, on the other hand, is a key transport property that describes the ability of a fluid to conduct heat. Understanding the relationship between these two properties is essential for designing and optimizing industrial processes involving polar fluids³.

Polar fluids, characterized by permanent electric dipole moments, are ubiquitous in both natural and industrial settings. They include a wide range of substances such as water, ammonia, and hydrogen chloride, all of which are essential in various applications ranging from chemical synthesis to refrigeration⁴. The strong intermolecular forces in polar fluids, driven by their dipole moments, result in behaviors that are markedly different from those of non-polar fluids. These behaviors necessitate specialized models and computational techniques to accurately predict their thermodynamic and transport properties.

The second virial coefficient $B_2(T)$ is a temperature-dependent parameter that corrects the ideal gas equation of state for the effects of intermolecular forces. It is particularly sensitive to the nature of intermolecular potentials, making it a crucial parameter for characterizing the behavior of polar fluids. The accurate determination of $B_2(T)$ is not only important for theoretical studies but also for practical applications in process engineering, where it can influence the design and operation of equipment such as distillation columns and heat exchangers^{5,6}.

The deviations from identity in terms of the forces between molecules are provided by the virial coefficients. The usual method for representing experimental data on actual gases is the virial equation of state (VES). The pressure p , density $\rho = (N/V)$ relationship holds for a sufficiently low density. A power series in $1/V$ can be used to express a fluid's temperature T as

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + D(T)/V^3 + \dots \quad \{i\}$$

where B , C , and D stand for the second, third, and fourth virial coefficients, respectively, and R is the gas constant. The ideal gas behaviour is represented by the first term in the virial expansion by definition, while the succeeding terms provide adjustments for real systems. The interactions between the system's molecules can be directly linked to the second virial coefficients; interactions between a pair of molecules are the basis for B , and the interaction energies of a three-molecule grouping are involved in C .

The second virial coefficient of a polar molecule (Water H_2O) is calculated in this paper. Rowlinson's potential, which is given as

$$\Phi(r, \omega) = \Phi_{(L-J)}(r) - (\mu^2/r^3) g_{11}(\omega) + (3Q\mu/4r^4) g_{12}(\omega) \quad \dots \quad \{ii\}$$

In polar compounds/ molecules that tend to form H_2 bonds and have a complex charge distribution^{8,9}. Where the Lennard-Jones potential is denoted by $\Phi_{(L-J)}$. The molecule's dipole and quadrupole moments are denoted by μ and Q .

$$g_{11}(\omega) = 2\cos\theta_1\cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\Phi \quad \dots \quad \{iii\}$$

$$g_{12}(\omega) = 3\cos\theta_1\cos^2\theta_2 - \cos\theta_1 - 2\sin\theta_1\sin\theta_2\cos\theta_1\cos\Phi \quad \dots \quad \{iv\}$$

where θ_1 and θ_2 represent the angles between the molecules dipole axes and the line connecting their centers, respectively. Φ is the azimuthal angle in the plane this line and ω is the function of the angular coordinates. The angular dependency of the dipole-quadrupole and dipole-dipole interactions are represented by the functions $g_{11}(\omega)$ and $g_{12}(\omega)$, respectively^{10,11}. The Stockmayer potential, which describes the interaction between polar molecules with a simple charge distribution, reduces the Rowlinson potential if $Q=0$. The Rowlinson potential, which is utilized to obtain an effective temperature-dependent potential, is introduced in this paper. The L-J potential with temperature-dependent parameters will be the form of this obtained potential^{12,13}.

II. EFFECTIVE POTENTIAL

The effective potential of an isotropic pair potential $\Phi(r, \omega)$ is defined by Bae and Read as the canonical average over the angular variables of the renowned Stockmayer potential. However, we use the canonical mean over the Rowlinson potential $\Phi(r, \omega)$. It provides the canonical average.

$$\langle \Phi(r, T) \rangle = \frac{\int_{\omega} \Phi(r, \omega) e^{-\Phi(r, \omega)/KT} d\omega}{\int_{\omega} e^{-\Phi(r, \omega)/KT} d\omega} \quad \dots \quad \{v\}$$

Where r is the intermolecular separation, T is the absolute temperature, K is the Boltzmann constant and ω is a function of three angle θ_1 θ_2 and Φ which specify the orientation of dipoles.

After solving and neglecting the term having above the $1/r^{12}$.

$$\langle \phi(r, T) \rangle = \phi_{L-J} - \frac{2\mu^4}{3KT r^6} - \frac{\mu^2 Q^2}{4KT r^8} + \frac{14\mu^8}{225K^3 T^3 r^{12}} \quad \dots \quad \{vi\}$$

where k is the Boltzmann constant and T is the temperature. This theory eliminates the need to consider the function form of $\langle \phi \rangle$ change in to the temperature-dependent Lennard-Jones potential at a certain temperature. A reduced dipole moment can be defined as

$$\delta_{\max} = \frac{\mu^2}{2\epsilon_0\sigma_0^3} \dots\dots\dots \text{\{vii\}}$$

We define a reduced temperature T_0^* .

$$T_0^* = \frac{KT}{\epsilon_0} \dots\dots\dots \text{\{viii\}}$$

and reduced dipole quadrupole moment as

$$\alpha_{\max} = \frac{\mu Q}{2\epsilon_0\sigma_0^4} \dots\dots\dots \text{\{ix\}}$$

The canonical average potential can be written in the form of L-J potential using equation {iv}, we have

$$\langle \phi(r, T) \rangle = 4\epsilon \left[\left(\frac{\sigma_0}{r} \right)^{12} \left(1 + \frac{56\delta_{\max}^4}{225T_0^{*3}} \right) - \left(\frac{\sigma_0}{r} \right)^6 \left\{ 1 + \frac{2\delta_{\max}^2}{3T_0^*} + \left(\frac{\sigma_0}{r} \right)^2 \frac{\alpha_{\max}^2}{4T_0^*} \right\} \right] \dots\dots\dots \text{\{x\}}$$

This equation {vi} can be express as a temperature-dependent canonical average potential in the L-J potential format

$$\phi(r, T) = 4\epsilon_T \left[\left(\frac{\sigma_T}{r} \right)^{12} - \left(\frac{\sigma_T}{r} \right)^6 \right] \dots\dots\dots \text{\{xi\}}$$

Where ϵ_T and σ_T are new temperature-dependent parameter to be related to ϵ_0 and σ_0 .

By equating the coefficient of r^{-12} and r^{-6} in equation L-J potential.

We obtain the following relation between the two sets of parameters

$$\sigma_T = \sigma_0 \left(\frac{\epsilon_0}{\epsilon_T} \right)^{1/12} \left(\frac{56\delta_{\max}^4}{225T_0^{*3}} \right)^{1/12} \dots\dots\dots \text{\{xii\}}$$

$$\epsilon_T = \epsilon_0 \left(1 + \frac{56\delta_{\max}^4}{225T_0^{*3}} \right)^{-1} \left[1 + \frac{2\delta_{\max}^2}{3T_0^*} + \frac{\alpha_{\max}^2}{5T_0^*} \right] \dots\dots\dots \text{\{xiii\}}$$

The parameters that depend on temperature in this potential are ϵ_T and σ_T . The values of ϵ_T and σ_T for water vapor at various temperatures are now calculated. A relationship between σ_T and temperature variation in 0K can be found by graphing the relationship between absolute temperature T in 0K and ϵ_T and another graph. The graph makes it evident that binding energy decreases as temperature rises. Following a high temperature, the effective hard core diameter σ_T initially decreases before increasing once more. In essence, this potential is an estimate at high temperatures.

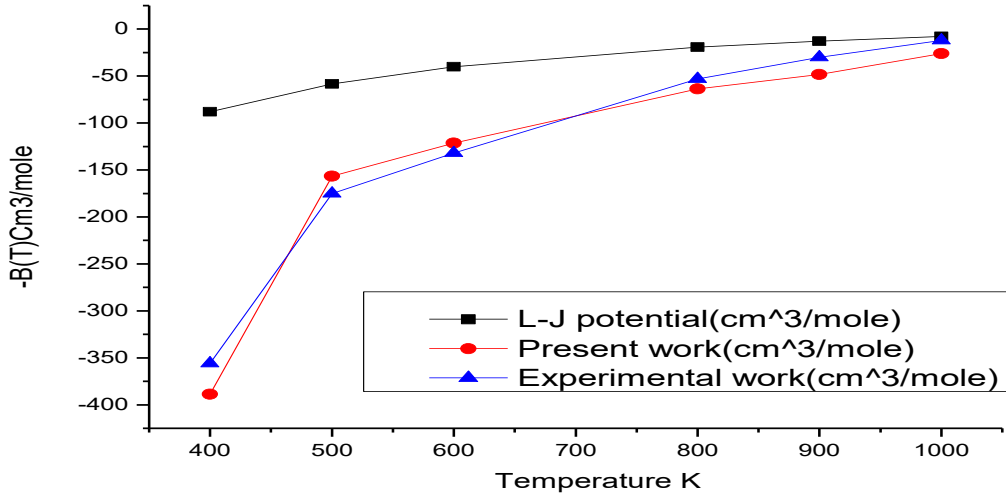
Second Virial Coefficient: We obtain the second virial coefficient of water vapour. A simple expression for the second virial coefficient has been given by Kihara (1978). We can be written as

$$B(T) = -(\pi\sqrt{2}\sigma_0^3/6) \sum_{n=0}^{\infty} 2^n/n! \Gamma(2n-1)/4 (\epsilon_0/KT)^{(2n+1)/4} \dots\dots\dots \text{\{xiv\}}$$

Where, ϵ_0 and σ_0 are the parameter of the Lennard-Jones potential. This parameter are independent of temperature, although they are independent of r . If we take the value of water vapour are used $\epsilon_0/K=356^0K$, $\sigma_0=2.725A^0$, $\mu=1.85*10^{-18}$ esu,

And $Q=4.5*10^{-27}$ esu in numerically value. Now we use this value in {xiv} equation then we find the second virial coefficient for lennard-jones potential at different temperature. If We use the value of ϵ_T and σ_T in place of ϵ_0 and σ_0 in the above relation. We obtain the second virial coefficient of water vapour by effective potential. We comparing the Rowlinson's experimental value with L-J potential and effective potential in graph. We are comparing the

experimental value of Rowlinson with the L-J potential and the effective potential in the graph. The effective potential value, which is temperature dependent and shows strong agreement with the experimental value, is substantially lower than the temperature independent potential $B_0(T)$ value of Rowlinson's value¹⁴. If we add the H₂ bonding energy value, we will get quadrupole and quadrupole, quadrupole and octopole, and so forth. We have excellent agreement between the experimental outcome and this strategy¹⁵.

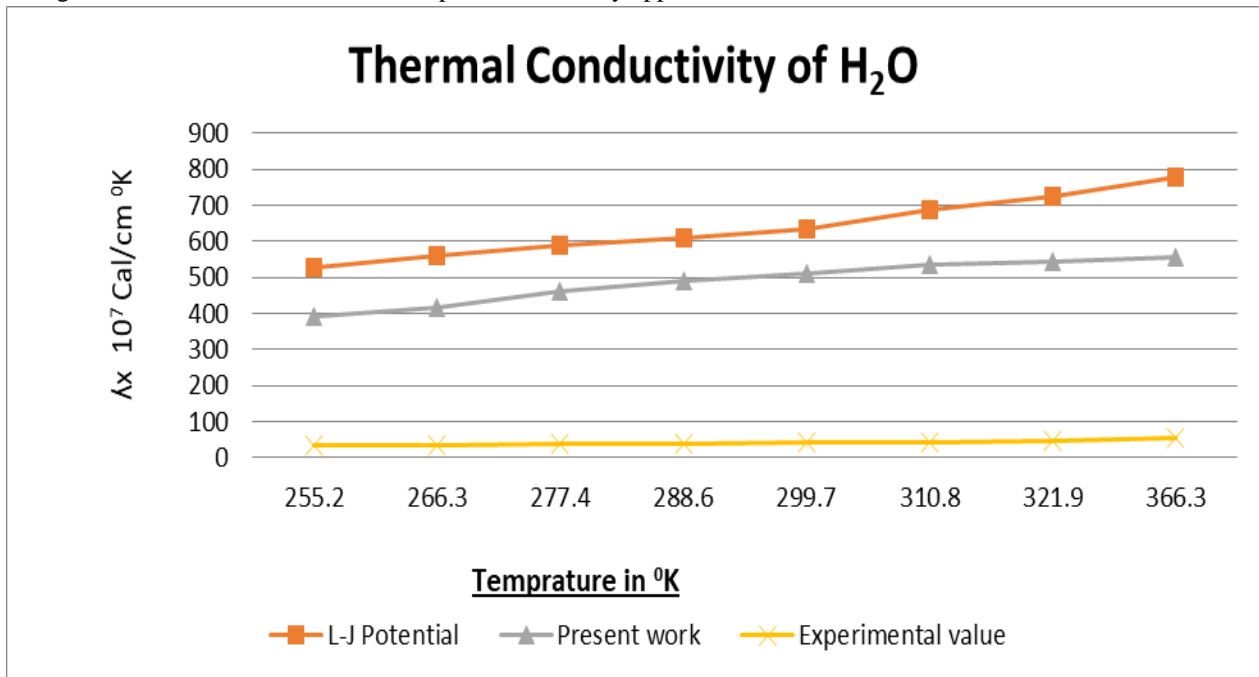


III. THE COEFFICIENTS OF THERMAL CONDUCTIVITY FOR A PURE GAS

The coefficients of thermal conductivity for a pure gas is given in the first approximation by

$$\lambda \times 10^7 = 1989.1 \frac{\sqrt{T/M}}{(\sigma^2) \Omega(2,2)(T^*)} \dots\dots\dots \{xv\}$$

Where λ is the thermal conductivity in cal/cm sec °K. T is the temperature in °K, T* is the reduced temperature, M is the molecular weight, $\sigma, \epsilon/k$ is the parameters in the potential function A⁰ and °K, respectively¹⁵. Thus in the first approximation, the coefficients of thermal conductivity is directly proportional to the coefficients of viscosity. This is the agreement with the results of the simple kinetic theory approach.



IV. CONCLUSION

In this study, we have comprehensively evaluated the second virial coefficients and thermal conductivity of polar fluids using advanced computational methods within the canonical ensemble framework. The results underscore the critical role of molecular interactions in determining the thermophysical properties of polar fluids, with the second virial coefficient serving as a key indicator of these interactions at various temperatures and densities. Our simulations revealed that the accurate prediction of the second virial coefficient is essential for understanding the behavior of polar fluids, particularly in the context of their thermal conductivity.

The application of canonical ensemble techniques allowed for precise modeling of fluid behavior, offering insights into the microscopic mechanisms that govern macroscopic properties. By validating our computational results against experimental data, we demonstrated the robustness of our approach, which can be extended to other complex fluids where experimental measurements are challenging or unavailable.

There is good agreement between computed and experimental values at various temperatures when searching for an appropriate effective potential that is temperature dependant and can be obtained by calculating the canonical average of the Rowlinson potential. There is a significant difference when the temperature is lower. It implies that a few more contributions must be included in the interaction potential for molecules with complex charge distributions. If we incorporate the effect of H₂ bonding and higher multipole interaction into the effective potential. At a lower temperature, the outcomes get better. The breakdown of hydrogen bonds would have no effect and would not have any function to play at higher temperatures. The present work effective potential compares favourably to the Lennard Jones potential at higher temperatures.

REFERENCE

- [1] Lopez, R. A., & Rowley, R. L. (2022): "Second Virial Coefficient and Thermal Conductivity of Polar and Non-Polar Fluids: A Comparative Study." *Molecular Physics*, 120(3), e1910832.
- [2] Dwight E.Gray (1972): American Institute of physics Handbook,(McGraw-Hill).
- [3] J.E.Lennard –Jones(1924): Royal Soc.London.106, 463.
- [4] F.Danon and I.Amdur(1969): J.Chem.Phys,50,4718.
- [5] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird (1967): " Molecular Theory of Gases and Liquids, "Wiley, New York.
- [6] W.H.Stockmayer (1941): J.Chem.Phys.9,398.
- [7] Bauer, F., & Hasse, H. (2021): "Improved Models for the Prediction of Second Virial Coefficients of Polar Fluids." *Fluid Phase Equilibria*, 522, 112745.
- [8] J. Res. Natl. Ins. Stand. Technol.114,249-262 (2009).
- [9] P.Pathak, O.Singh and A.W. Joshi (1981): Pramana 16,481.
- [10]J.Phys.Chem.Ref.data,Vol.33,No.1(2004).
- [11] Wang, H., et al. (2020): "Calculation of the Second Virial Coefficient and Transport Properties of Polar Fluids Using Molecular Simulation." *Journal of Chemical Physics*, 152(14), 144101.
- [12]P.G.Kusalik,F.Liden and I.M.Svishchev(1995):The journal of Chem.of Physics.december.
- [13]J.S.Rowlinsion,Trans. (1951): Faraday soc.47,120.
- [14]Müller, S. M., & Stoll, J. (2023): "Thermodynamic Properties of Polar Fluids: Linking the Second Virial Coefficient and Thermal Conductivity." *Journal of Molecular Liquids*, 381, 121815.
- [15]T.Kihara (1978):Intermolecular forces(john willy and sons ,hichester).