# A MICROSCOPIC STUDY OF Ne-Ne INTERACTIONS WITH PHENOMENOLOGICAL POTENTIALS USING SECOND VIRIAL COEFFICIENTS

Amal F. Al-Maaitah

Department of Physics, Mu'tah University, Al-Karak, Jordan

E-mail:amal.almaaitah@yahoo.com

**ABSTRACT:** The interactions of neon gas atoms are studied over a wide in the temperature-range 20–2400 K. An approach for the calculation of classical second virial coefficients for neon is described. Also, the first quantum corrections of the classical second virial coefficients are calculated for T < 100K. The results are undertaken using a family of semiphenomenological potentials that describe the interactions in neon gas atoms. The Boyle's and Joule inversion temperatures are determined. The results are combined with experimental second virial data to investigate the interactomic potentials of neon. The agreement between experimental and calculated values of Boyle's and Joule inversion temperatures is excellent for SAAP potential.

Keywords: Classical second virial coefficient, first quantum correction of the classical second virial coefficient, neon, Boyle's temperature, Joule inversion temperature.

### 1. INTRODUCTION

The macroscopic properties of materials are determined by the nature of interactions between their constituent atoms or molecules [1]. In most instances, the dominant contribution from such interatomic or intermolecular interactions can be attributed to the sum of interactions between all of the different pairs of atoms or molecules, i.e., two-body interactions. The pairwise interaction between neon atoms possesses many of the features displayed by other rare gas atoms. For neon, it is the closed 2p shell that simultaneously accounts for the weakly attractive longrange forces and the strongly repulsive short-range valence forces. Information regarding two-body interactions is accessible via experimental properties such as second virial coefficients or viscosities of dilute gases. From a theoretical perspective, two-body interactions can be evaluated via molecular simulation [2].

The second virial coefficient B is a function of the temperature T. It is an important parameter that characterizes the interparticle interactions. Positive B reflects predominantly repulsive interatomic interactions; whereas negative indicates predominantly attractive interaction [3]. Also, it can be considered as a link between the microscopic properties and the macroscopic properties of the system [4]. Furthermore, it can be considered as an indicator of the borderline between the classical and quantum regimes [5].

The importance of the second virial coefficient arises from its role in determining the thermodynamic properties of the system as well as exploring its degree of 'nonideality'. The thermodynamic properties of <sup>20</sup>Ne gas– the Helmholtz free energy, total internal energy, entropy, and specific heat capacity were calculated with the HFD-B binary potential in the temperature-range 27-36 K using the Galitskii-Migdal–Feynman (GMF) formalism [6]. Clusterization of <sup>20</sup>Ne gas is predicted at very low-temperature T~500  $\mu$ K. It was found that the second virial coefficient may be used as a predictor of the formation of small Ne clusters [7].

A few methods were applied for calculating the scattering and thermodynamic properties of neon gas, with several interatomic potentials. These methods include the localdensity approximation [8] and Monte-Carlo simulations [9]. Most of the semi phenomenological potentials [10-13] in present work are piecewise analytic functions of the interatomic separation r, which incorporate either or both of the theoretically determined short-range and long-range limits, and which exploit some empirical fit to interpolate between these two limits.

The current study presents a theoretical comparison of the classical second virial coefficient calculated using four of the semiphenomenological potentials that describe the interactions in the neon gas atoms. Also, the first quantum corrections of classical second virial coefficients,  $B_{qc}$  are calculated in the temperature-range 20-100 K. We obtain the Boyle's temperature ( $T_B$ ) and Joule inversion temperature ( $T_i$ ) for neon using the computed classical second virial coefficient of the various model potentials.

The four neon model potentials are discussed in Section 2. The classical second virial coefficient and the first quantum correction are outlined in Section 3. The results follow in Section 4; they are displayed in figures and tables, then discussed thoroughly and compared to previous results. Finally, the paper closes with a general Conclusion (Section 5).

#### 2. The Semiphenomenological Potentials

In the present work, we shall use four forms of different Ne-Ne potentials which accurately reproduce the potential energy at all inter-atomic separations:

# a) Lennard –Jones Potential:

The Lennard-Jones potential (also termed the L-J potential, 6-12 potential, or 12-6 potential) is a mathematically simple model that approximates the interaction between a pair of neutral atoms or molecules. The most common expression of the L-J potential is [10]

$$U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$
(1)

where  $\varepsilon$  is the depth of the potential well,  $\sigma$  is the finite distance at which the inter-particle potential is zero, r is the distance between the particles. This potential has a minimum value of  $-\varepsilon$  at  $r = 2^{\frac{1}{6}} \sigma$ . For Ne gas, appropriate values of  $\varepsilon = 35.6$  K and  $\sigma = 2.75$ Å.

b) Morse Potential:

The Morse potential approximates the potential energy of a vibrating diatomic molecule as a function of r, the distance of separation of its constituent atoms, and is given by [11]

$$V(\mathbf{r}) = \varepsilon [\exp\{-2C(\mathbf{r} - \mathbf{r}_{\mathrm{m}})\} - 2\exp\{-C(\mathbf{r} - \mathbf{r}_{\mathrm{m}})\}]$$
(2)

where  $\varepsilon$  is the depth of the potential energy minimum where  $r = r_m$  and the constant C is related to the curvature of the potential at its minimum. For Ne gas,  $\epsilon = 44.6$  K,  $r_m = 3.0446$  Å and C=1.85 Å<sup>-1</sup>. c) The HFD-B3 potential:

The principal features of the HFD-B3 potential are: (i) a strongly-repulsive, short-range component arising from the Pauli exclusion principle as the electronic clouds of the two interacting atoms begin to overlap strongly; (ii) a weaklyattractive tail, thanks to Van der Waals' forces, which can be viewed as a multipole expansion reflecting the interaction between the polarization fields associated with the interacting atoms; (iii) a minimum in between denoting equilibrium. It is given by [12] --\*()

$$\mathbf{V}(\mathbf{r}) = \varepsilon \mathbf{V}^*(\mathbf{x})$$

$$V^{*}(x) = A \exp(-\alpha x + \beta x^{2}) - \left\{ \frac{C_{6}}{x^{6}} + \frac{C_{8}}{x^{8}} + \frac{C_{10}}{x^{10}} \right\} F(x)$$
(4)

(3)

$$F(x) = \begin{cases} exp \left[ -\left\{ \frac{D}{x} - 1 \right\}^2 \right], & x < D \\ 1, & x \ge D \end{cases}$$
(5)

$$x \equiv \frac{r}{r_m}$$

The parameters for Ne-Ne potential are tabulated in Table 1.

Table 1: Parameters for Ne-Ne HFD-B3 potential.

Parameters	HFD-B3	
А	8.9571795×10 <sup>5</sup>	
r <sub>m</sub>	3.091Å	
3	42.25K	
D	1.36	
α	13.86434671	
β	-0.12993822	
C <sub>6</sub>	1.21317545	
C <sub>8</sub>	0.53222749	
C <sub>10</sub>	0.24570703	

d) Simplified ab initio atomic potential (SAAP):

The simplified ab initio atomic potential containing a constant negative term, plus an exponential term with a small decrement for the attractive well, plus an exp(r)/rterm with a large decrement for the repulsion zone. It is given by [13]:

$$u_{SAAP} = \varepsilon \left[ \frac{\left(\frac{a_0 \sigma}{r}\right) \exp\left[\left(a_1 / \sigma\right) r\right] + a_2 \exp\left[\left(a_3 / \sigma\right) r\right] + a_4}{1 + a_5 (r / \sigma)^6} \right]$$
(6)

The parameters for Ne gas are summarized in Table 2.

Sci.Int.(Lahore),32(1),-1-6,2020 Table 2. Parameters for No-No SAAP notantial

Table 2. I afailleters for the the SAAT potential.			
Parameters	SAAP		
ε	42.3616508K		
σ	2.759124561Å		
$a_0$	211781.8544		
<i>a</i> <sub>1</sub>	-10.89769496		
<i>a</i> <sub>2</sub>	-20.94225988		
<i>a</i> <sub>3</sub>	-2.317079421		
$a_4$	-1.854049559		
$a_5$	0.7454617542		

#### 3. Second Vrial Coefficient

The classical second virial coefficient  $B_{cl}$  (T) and the corresponding first quantum correction  $B_{qc}\left(T\right)$  of a system

of particles are given by [14] 
$$B_{cl}(T) = 2\pi \int_{0}^{\infty} \left[1 - e^{-\beta V(r)}\right] r^2 dr$$
  
. (7)

$$B_{qc}(T) = \frac{\pi \hbar^2 \beta^3}{6m} \int_0^\infty \left[ e^{-\beta V(r)} \right] V'(r)^2 r^2 dr , \qquad (8)$$

where V(r) is the binary interatomic potential, V'(r) is its first derivative with respect to the argument r, which is the magnitude of the interatomic separation, and  $\beta$  is the temperature parameter (k<sub>B</sub> T)<sup>-1</sup>, k<sub>B</sub> being Boltzmann's constant.

## 4. RESULTS AND DISCUSSION

#### 4.1 Second Virial Coefficients at Low Temperatures

Our results for the classical second virial coefficient B<sub>cl</sub>, in the temperature range 20-100 K are displayed in Figure1, and in Table 3 using four potentials: Lennard –Jones, Morse, HFD-B3, and SAAP potentials. The corresponding results for the first quantum correction  $B_{qc}$  are shown in Table 4. In the low T-limit, where the attractive part of the interaction potential for neon atoms dominates, B<sub>cl</sub> is large and negative. It increases as T increases, becoming less negative. At low T The mean energies of the atoms in the gas are of the same order of magnitude as the depth of the potential well; so that the interacting atoms spend most of their time in the attractive region of the potential. This results in a decrease in the gas pressure which leads to a negative B<sub>cl</sub>[15].

Although the previous figure displayed a similar behavior for classical second virial coefficients using investigation of this our potentials, a further coefficient showed that there is a deviation at T <40K. This deviation arises from quantum effects in the low-temperature limit, i.e., quantum effects become important at T < 40 K.

On the other hand, the first quantum correction  $B_{\rm qc}$  is predominantly positive and decreases with increasing T. This means that quantum character disappears gradually with increasing temperature.



# Figure 1: The classical second virial coefficient $B_{cl}$ [cm<sup>3</sup>/mole] as obtained from the calculation of this work using L-J potential, Morse potential, the HFD-B3 potential, and SAAP potential in the T-range 20-100 K.

By comparing  $B_{cl}$  and  $B_{qc}$  (Tables 3 and 4), it is found that the quantum corrections have major importance in the 'low'-temperature regime.

Fable 3: The classical second virial coefficient, B <sub>cl</sub>	cm <sup>3</sup> /mole] in the temperature -range 20-100 K.
---	--

		B <sub>cl</sub> [cm <sup>3</sup> /mole]		
Т	L-J	Morse	HFD-B3	SAAP
20	-183.217	-235.125	-222.723	-219.181
30	-89.4423	-103.167	-102.438	-100.630
40	-54.1544	-59.8387	-60.6017	-59.3936
50	-35.8268	-38.8577	-39.6763	-38.7645
60	-24.6621	-26.6176	-27.2067	-26.470
70	-17.1791	-18.6541	-18.9691	-18.3474
80	-11.8339	-13.0894	-13.1447	-12.6041
90	-7.83779	-9.00011	-8.82378	-8.3432
100	-4.7465	-5.88072	-5.50122	-5.06687

Table 4: The first quantum correction to classical second virial coefficient,  $B_{qc}$  [cm<sup>3</sup>/mole] in the temperature -range 20-100 K.

	B <sub>qc</sub> [cm <sup>3</sup> /mole]				
Т	L-J	Morse	HFD-B3	SAAP	
20	316.8818	478.036	484.8611	496.044	
30	97.71184	121.3295	130.6136	133.348	
40	48.73924	54.19209	60.47079	61.6556	
50	30.18806	31.198	35.68325	36.3448	
60	21.0689	20.65077	24.05717	24.4815	
70	15.83888	14.90577	17.61572	17.9124	
80	12.51968	11.40423	13.63584	13.8555	
90	10.25757	9.094989	10.98147	11.151	
100	8.632521	7.480951	9.10848	9.24346	

#### 4.2 Second Virial Coefficients at High Temperatures

The results for  $B_{cl}$ , in the temperature range 50-2400 K are displayed in Figure 2. The experimental data are also shown in this figure.  $B_{cl}$  shows good agreement with the experimental values. Calculated values using our potentials are compared with the experimental data in Table 5.  $B_{cl}$  increases as T increases, becoming less negative. At high T,

the average energies of the atoms increase; so that the predominant contribution to  $B_{cl}$  arises from the repulsive portion of the potential. This causes an increase in the gas pressure and, hence,  $B_{cl}$  becomes less negative [15].

At a certain  $T \equiv T_B$  (Boyle's temperature),  $B_{cl} = 0$ . This occurs when the attractive forces balance exactly the repulsive forces. For  $T > T_B$ ,  $B_{cl}$  becomes positive.

Negative (positive) second virial coefficient means that the overall interaction is attractive (repulsive).  $B_{cl}$  continues to increase with increasing T, until it attains a maximum value; after which it decreases. Maximum  $B_{cl}$  occurs at the Joule inversion temperature Ti, associated with the Joule free expansion. For  $T > T_i$ , it changes relatively slowly. The potential accuracy can be tested by computing the Boyle temperature  $T_B$ . The Boyle temperature  $T_B$  is a

characteristic of two-body potential. This indicates that the interatomic potential, which does not accurately predict  $T_B$ , is inaccurate.  $T_B$  and  $T_i$  are given in Table 6 together with previous results. Our results are in good agreement with those. Clearly, from Table 6 the excellent agreement of SAAP potential with that of experimental data for  $T_B$  and  $T_i$  than other used potentials

able 5: The classical second virial coefficient B <sub>cl</sub> [cm	n <sup>3</sup> /mole] in the temperature -range 50-2400 K with previous experimental
	data.

	B <sub>el</sub> [cm <sup>3</sup> /mole]				
T [K]	L-J	Morse	HFD-B	SAAP	Exp.
50	-35.82	-38.86	-39.67	-38.76	-35.40
60	-24.66	-26.62	-27.2	-26.47	-24.90
70	-17.18	-18.66	-18.96	-18.34	-17.10
80	-11.83	-13.09	-13.14	-12.6	-12.80
100	-4.75	-5.88	-5.5	-5.06	-6
150	3.89	2.6	3.68	3.99	3.20
200	7.76	6.26	7.74	7.99	7.70
250	9.88	8.19	9.93	10.15	10
300	11.16	9.32	11.25	11.44	11.30
350	11.99	10.03	12.1	12.27	12.10
400	12.56	10.5	12.66	12.82	12.70
450	12.95	10.8	13.05	13.2	13.10
500	13.23	11.01	13.32	13.47	13.40
550	13.43	11.13	13.51	13.65	13.70
600	13.58	11.21	13.64	13.77	13.62
700	13.75	11.28	13.78	13.91	13.77
800	13.83	11.27	13.83	13.95	13.87
900	13.85	11.21	13.82	13.93	13.91
1000	13.83	11.12	13.77	13.87	13.88
1200	13.73	10.91	13.62	13.72	13.75
1400	13.6	10.69	13.43	13.52	13.61
1600	13.45	10.46	13.24	13.32	13.46
1800	13.3	10.24	13.04	13.12	13.31
2000	13.15	10.03	12.85	12.92	13.16
2400	12.86	9.65	12.48	12.55	12.87



Figure 2: The classical second virial coefficient  $B_{cl}(T)$  [cm<sup>3</sup>/mole] as a function of temperature T [K], as from experiment and from the calculation of this work using L-J potential, Morse potential, the HFD-B3 potential, and SAAP potential.

#### CONCLUSION

The classical second virial coefficient, B<sub>cl</sub> provides valuable information about the interatomic forces. Using four types of interatomic pair potentials (Lennard -Jones, Morse, HFD-B3, and SAAP), Bcl for neon gas is calculated over a wide range of temperatures. The results are compared with the experimental values of neon gas. The agreement is good. At high temperature ( $T \ge 120$  K), where the repulsive part of the interaction dominates, B<sub>cl</sub> is positive. However, at low temperatures (T  $\leq$ 120 K), where the attractive part of the interaction dominates, B<sub>cl</sub> is negative. Also, the first quantum corrections of classical second virial coefficients are calculated in the temperature-range 20-100 K. The temperature at which  $B_{cl} = 0$  is called the Boyle's temperature T<sub>B</sub>. The maximum value of B<sub>cl</sub> occurs at the inversion temperature Ti. associated with the Joule free expansion. The excellent agreement of SAAP potential with that of experimental data for T<sub>B</sub> and T<sub>i</sub> than other used potentials is noted.

Table 6: Boyle's temperature T<sub>B</sub> [K] and Joule inversion temperature T<sub>i</sub> [K]. Previous results are included for comparison purposes.

	L-J	Morse	HFD-B	SAAP	Previous results
T <sub>B</sub> [K]	121.7	129.02	124.1	120.1	120.32 <sup>a</sup>
T <sub>i</sub> [K]	900	726	822	860	867 <sup>b</sup>

a) [16] b) [17]

#### REFERENCES

[1] C. G. Gray and K. E. Gubbins, Theory of Molecular Fluids Vol. 1: Fundamentals (Clarendon Press, Oxford, 1984).

[2] R. J. Sadus, Molecular Simulation of Fluids: Theory, Algorithms and Object-Orientation (Elsevier, Amsterdam), 1999.

[3] A. F. Al-Maaitah, Thermodynamic Properties of Argon Gas in the Temperature-Rang 100-3000 K, Science International (Lahore), 31(3), 45-44 (2019).

[4] J. van Rijssel, V.F.D. Peters, J.D. Meeldijk, R.J. Kortschot, R.J.A. van Dijk-Moes, A. V. Petukhov, B.H. Erné, A.P. Philips, J. Phys. Chem. B 118 (2014) 11000.

[5] H. B. Ghassib, A. S. Sandouqa, B. R. Joudeh, S. M. Mosameh, Can. J. Phys. 92(9), 997-1001 (2014).

[6] A .N. Akoura, A.S. Sandouqab, B.R. Joudeh, H.B. Ghassibe, Equation of State of 20Ne gas in the temperature-range 27–36 K, Chinese Journal of Physics 56 411–422 (2018).

[7] A. F. Al-Maaitah, A. S. Sandouqa, B. R. Joudeh, and O.T. Al-Obeidat, The Scattering and thermodynamic

Properties of Ultracold <sup>20</sup>Ne Vapor, Chinese Journal of Physics, , 62,194-201 (2019).

[8] Shi, Hualin., and Zheng, Wei-Mou., Thermodynamic Properties of a Trapped Interacting Bose Gas. Physics A 258 (1998) 303-310.

[9] Nasrabad, A.E., Laghaei, R. and Deiters, U.K., Prediction of the Thermophysical Properties of Pure Neon, Pure Argon, and the Binary Mixtures Neon-Argon and Argon-Krypton by Monte Carlo Simulation Using ab initio Potentials, Journal of Chemical Physics 121 (2004) 6423-6434.

[10] Artit Hutem and Sutee Boonchui, J Math Chem 50:1262–1276 (2012).

[11] H. R. Glyde, Anharmonicity and potentials for the solidified inert gases, J. Phys. C: Solid State Phys. (1970) 03 810.

[12] Aziz, R. A, and Slaman, M. J., The Ne-Ne Interatomic Potential Revisited, *Chem. Phys.*, 130 187 (1989).

[13] Ulrich K. Deiters1 and Richard J. Sadus, Two-body interatomic potentials for He, Ne, Ar, Kr, and Xe from ab initio data, J. Chem. Phys. 150, 134504 (2019).

[14] A. A. Al Ajaleen, A.S. Sandouqa, and H.B. Ghassib, The second virial coefficient for Rubidium-87 (<sup>87</sup>Rb) gas in the temperature range 1000-40000 K and beyond, British Journal of Science, Vol. 17 (1) (2019).

[15] P. J. Gans, Real Gases. Physical Chemistry 1, 25, 0651-0662 (1994).

[16] R. S. Katti, R.T. Jacobsen, R.B. Stewart, M. Jahangiri, Adv. Cryo. Eng. 31(1986) 1189–1197.

[17] E. Albarrán-Zavala, B. A. Espinoza-Elizarrarazand F. Angulo-Brown, Joule Inversion Temperatures for Some Simple Real Gases. The Open Thermodynamics Journal, 2009, 3, 17-22.