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Validation of the applicability of the ideal gas equation of state and its correction based on molecular simulation and statistical methods

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Abstract. The ideal gas equation of state is a theoretical model devised to simplify the behaviour of real gases, although its usefulness is limited in numerous realistic scenarios. The experimental subject of this study is the Ar atomic gas, and data is gathered using molecular simulation techniques to assess the suitability and scope of the ideal gas equation of state. Simultaneously, statistical techniques such as linear regression and polynomial regression are employed to construct a novel model. Additionally, the ideal gas equation of state is adapted under specific circumstances, leading to the proposition of a fresh empirical gas equation of state. The study determined that the ideal gas equation of state can be applied to Ar atomic gases within the temperature range of 300-500 K and gas densities ranging from 0.1-0.6 g/cm^3. However, when examining higher gas densities, specifically at temperatures of 300 K and densities exceeding 0.6 g/cm^3, a new empirical gas equation was derived. This equation demonstrates that the pressure of Ar atomic gas is influenced by the 1st and 6th power terms of its density.

Keywords: Molecular Simulation, Ideal Gas Equation, Statistic, Physics, Regression Model.

1. Introduction

Numerous researchers have endeavored to ascertain the optimal equation capable of describing the condition of a gas. There exists a multitude of study studies and alterations pertaining to the ideal gas equation of state. Presently, the number of gas equations has surpassed 100, assuming a significant part in both theoretical investigations and practical implementations [1-2]. The modified gas equations can be categorized into three main groups based on the methods employed in their derivation. These groups include semi-empirical and semi-theoretical equations, exemplified by the Van der Waals equation, theoretical equations, such as the Virial equation, and empirical equations of state, such as the Beattie-Bridgeman equation, among others [3-4]. However, no one equation of state has yet been able to be altered by a perfect equation of state. It is not feasible to employ a single equation of state to address all practical challenges encountered with gases. In the context of engineering, it is crucial to identify and utilize the appropriate equation of state for gases that is suitable inside the relevant state, taking into consideration the specific characteristics of the given application [5-7].

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The ideal gas equation is a mathematical expression that elucidates the interplay between pressure, volume, and temperature of an ideal gas in a state of equilibrium. Its fundamental form can be expressed as:

$$PV = nRT \tag{1}$$

Where P is the pressure (Pa), V is the volume of the gas (m^3), T is the temperature (K), n is the amount of substance of the gas (mol), and R is the molar gas constant (J/(mol.K)).

The concept of an ideal gas is a theoretical construct devised to simplify the behavior of real gases, and its suitability is limited in numerous real-world scenarios. The ideal gas exhibits two fundamental characteristics: Molecules, in and of themselves, do not occupy a significant volume and exhibit minimal intermolecular interactions. In practical scenarios, gases that are not subjected to extremely low temperatures or high pressures can be approximated as ideal gases. It is observed that as the temperature increases and the pressure decreases, the behavior of the gas becomes increasingly similar to that of an ideal gas [8].

The primary methodology employed in this study involves the utilization of the Moldy molecular simulation system to get experimental data through simulation. Moldy is a software application designed for the purpose of conducting molecular dynamics simulations on condensed matter systems. This computational method is capable of effectively handling a wide range of stiff polyatomic compounds, including atoms, ions, and their many combinations. The computational approach employed in this study involves the utilization of the link cell method for the computation of short-range forces, while the Ewald sum methodology is employed to effectively manage long-range electrostatic forces. The simulation of the dynamic values of energy, temperature, pressure, and other physical quantities in the system can be achieved by inputting the fundamental physical parameters of the simulated object and configuring the control parameters.

This study focuses on the experimental investigation of Argon as the subject of analysis. The Moldy molecular simulation method is employed to conduct molecular simulation calculations of Ar atomic gases at varying temperatures and molecular densities. The objective is to acquire data pertaining to energy, pressure, and other physical properties within the simulated system. The purpose of this analysis is to assess the suitability and range of applicability of the ideal gas equation of state. Furthermore, the data acquired from the molecular simulation will be subjected to statistical analysis in this research. The ideal gas equation of state will be refined by developing a novel regression model employing techniques such as linear regression, polynomial regression, and other relevant models. Additionally, this study aims to propose an empirical equation of state suitable for Argon atoms in a specific state by fitting experimental data.

2. Verification of the equation

2.1. Formula deformation

From the ideal gas equation of state, it can be deduced that when the density of the gas in the control system is constant, the pressure and temperature of the gas are theoretically proportional to:

$$p = \frac{nR}{V} \cdot T$$

$$\text{Oder } P = \frac{m}{V} = \frac{n \cdot \mu}{V} \text{ get } P = \rho \frac{R}{\mu} \cdot T \tag{2}$$

In the equation (2), where ρ denotes the gas density and μ denotes the molar mass of the gas molecules.

DOI: 10.54254/2755-2721/58/20240679

2.2. Temperature range verification

2.2.1. Molecular simulation. In this study, the Moldy molecular simulation system was used to input the basic physical parameters of Ar atoms into the file argon.in and set the initial parameters of the simulation system into the file control.argon, control the density of the gas to 0.1 g/cm^3, and the temperature to be set at intervals of 50 K from 50-1000 K, to carry out molecular simulation for a number of times and to record the simulation data obtained.

Obtain the actual simulated pressure value P_1. Calculate the pressure value P_0, and the absolute deviation of the two $\Delta P = P_1 - P_0$, and the relative deviation RD (Table 1).

Table 1. Simulated data at 50-1000 K.

Serial number	Atom	ρ (g/cm^3)	T (K)	P_1 (MPa)	P_0 (MPa)	ΔP (MPa)	RD (%)
1	Argon	0.1	50	0.588	1.04	-0.452	-43.46
2	Argon	0.1	100	1.51	2.08	-0.57	-27.40
3	Argon	0.1	150	2.51	3.12	-0.61	-19.55
4	Argon	0.1	200	3.71	4.16	-0.45	-10.82
5	Argon	0.1	250	4.85	5.2	-0.35	-6.73
6	Argon	0.1	300	5.94	6.24	-0.3	-4.81
7	Argon	0.1	350	7.07	7.28	-0.21	-2.88
8	Argon	0.1	400	8.23	8.32	-0.09	-1.08
9	Argon	0.1	450	9.47	9.37	0.1	1.07
10	Argon	0.1	500	10.5	10.41	0.09	0.86
11	Argon	0.1	550	11.9	11.44	0.46	4.02
12	Argon	0.1	600	12.7	12.48	0.22	1.76
13	Argon	0.1	650	14	13.52	0.48	3.55
14	Argon	0.1	700	14.9	14.56	0.34	2.34
15	Argon	0.1	750	16.3	15.6	0.7	4.49
16	Argon	0.1	800	17.3	16.64	0.66	3.97
17	Argon	0.1	850	18.5	17.68	0.82	4.64
18	Argon	0.1	900	19.4	18.72	0.68	3.63
19	Argon	0.1	950	20.9	19.76	1.14	5.77
20	Argon	0.1	1000	21.9	20.8	1.1	5.29

The simulation results were used to generate plots of the P-T curve, as well as the ΔP-T and RD-T curves (Figs. 1, 2, 3). These plots were constructed with temperature as the independent variable on the horizontal axis and pressure as the dependent variable on the vertical axis. The purpose of these plots was to facilitate a comparison between the pressure values acquired from the simulation and the corresponding theoretical pressure values.

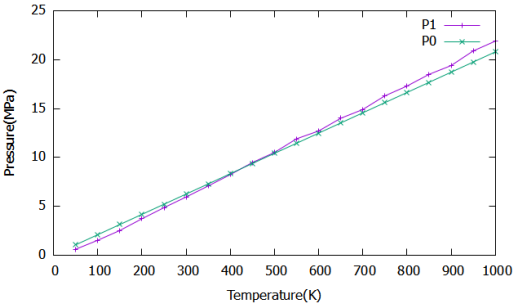

Figure 1. P1-T curve at density of 0.1 g/cm^3.

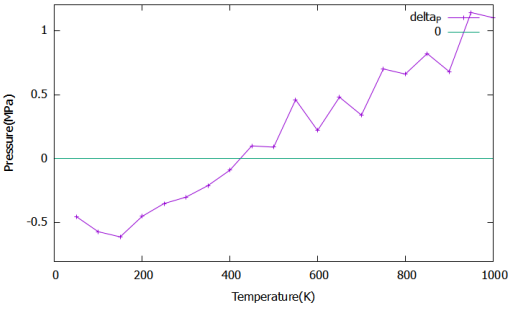

Figure 2. ΔP-T curve at density of 0.1 g/cm^3.

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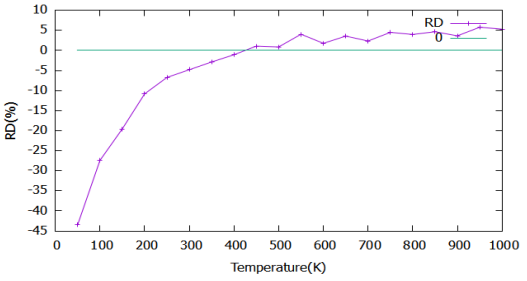

Figure 3. RD-T curve at density of 0.1 g/cm^3.

The investigation reveals that the absolute deviation between the observed simulated value and the theoretically calculated value remains relatively small within the temperature range of 0-1000 K. Additionally, the two curves representing P_1 and P_0 exhibit a significant degree of overlap, indicating a clear linear relationship. These findings suggest that the ideal gas equation of state is generally applicable when the gas density is 0.1 g/cm^3. Within the temperature range spanning from 300 K to 500 K, it is seen that the disparities between the actual and theoretical pressure values exhibit minimal absolute and relative variations. Moreover, the theoretical equations employed in this context provide a notable degree of precision in predicting these pressure values.

2.2.2. Linear regression. In order to obtain more data for further linear regression and data analysis, molecular simulations were performed again at 10 K intervals in the temperature range of 300-500 K. The results were as follows (Table 2).

Table 2. Simulated data at 300-500 K for linear regression.

Serial number	Atom	ρ(g/cm^3)	T(K)	P_1(MPa)	P_0(MPa)
1	Argon	0.1	300	5.94	6.24
2	Argon	0.1	310	6.17	6.45
3	Argon	0.1	320	6.56	6.66
4	Argon	0.1	330	6.73	6.86
5	Argon	0.1	340	6.81	7.07
6	Argon	0.1	350	7.07	7.28
7	Argon	0.1	360	7.49	7.49
8	Argon	0.1	370	7.77	7.70
9	Argon	0.1	380	7.86	7.90
10	Argon	0.1	390	8.14	8.11
11	Argon	0.1	400	8.23	8.32
12	Argon	0.1	410	8.26	8.53
13	Argon	0.1	420	8.71	8.74
14	Argon	0.1	430	8.84	8.94
15	Argon	0.1	440	9.21	9.15
16	Argon	0.1	450	9.47	9.36
17	Argon	0.1	460	9.7	9.57
18	Argon	0.1	470	10.1	9.78
19	Argon	0.1	480	10.2	9.98
20	Argon	0.1	490	10.3	10.19
21	Argon	0.1	500	10.5	10.40

Linear regression analysis was performed to obtain (Table 3, Fig. 4):

DOI: 10.54254/2755-2721/58/20240679

$$y = \alpha + bx$$

Table 3. Regression Parameters.

Parameters	Parameter Values	Asymptotic Standard Error	Relative Standard Error
a	-0.892208	±0.1624	18.2%
b	0.0229519	±0.0004014	1.749%

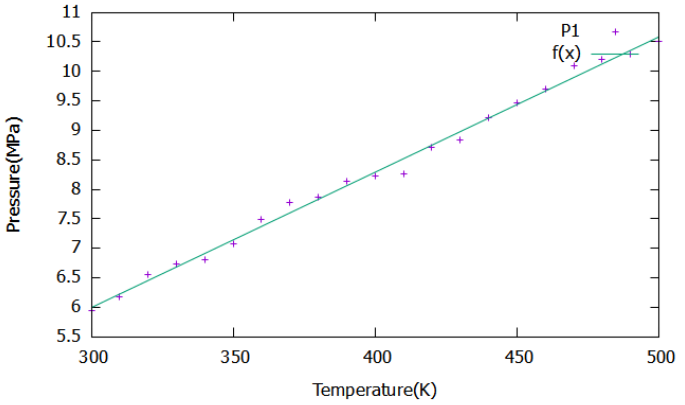

Figure 4. Linear regression ($y = a + bx$) at $300 - 500$K.

From the results, it is found that the standard error of the intercept a parameter is large, and according to the form of the ideal gas equation of state, the intercept should be 0. Therefore, the intercept is removed, and the linear regression is performed again with $y = cx$, and the results are as follows (Table 4, Fig. 5):

$$y = cx$$

Table 4. Regression Parameters.

Parameters	Parameter Values	Asymptotic Standard Error	Relative Standard Error
c	0.0207714	±0.9.422e-05	0.4536%

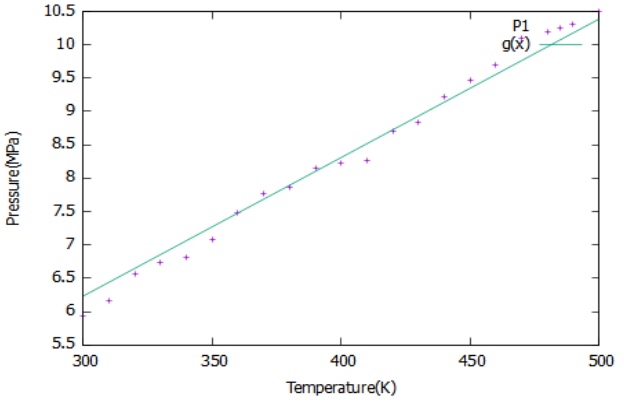

Figure 5. Linear regression ($y = cx$) at $300 - 500$ K.

From the regression results, it is found that the linear relationship between pressure P and temperature T in the temperature range of 300-500 K is better when the density of gas is controlled to be 0.1 g/cm^3. And the regression results are very close to the theoretical formula (substituting the gas density $\rho = 0.1$ g/cm^3 into the formula to get the specific value): $p = 0.0208 \cdot T$

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Therefore, the ideal gas equation of state is fully applicable at density 0.1 g/cm^3 and temperature 300-500K.

2.3. Density range verification

The above part have partially verified the temperature range over which the ideal gas equation of state is applicable at a relatively low gas density, verifying the applicability of the equation at lower gas densities. In order to investigate the applicability of the ideal gas equation of state under other conditions of different gas densities, the temperature is now set to 300 K, and the gas density from 0.1-1.0 g/cm^3, and several molecular simulations are carried out to obtain the system's pressure and other physical quantities parameters under different density conditions (Table 5).

Table 5. Simulated data at 0.1-1.0 g/cm^3.

Serial number	Atom	ρ(g/cm3)	T(K)	P_1(MPa)	P_0(MPa)	ΔP(MPa)	RD(%)
1	Argon	0.1	300	5.98	6.24	-0.26	-4.17
2	Argon	0.2	300	11.4	12.48	-1.08	-8.65
3	Argon	0.3	300	17.2	18.72	-1.52	-8.12
4	Argon	0.4	300	23.6	24.96	-1.36	-5.45
5	Argon	0.5	300	30.7	31.2	-0.5	-1.60
6	Argon	0.6	300	38.5	37.44	1.06	2.83
7	Argon	0.7	300	50.2	43.68	6.52	14.93
8	Argon	0.8	300	67.8	49.92	17.88	35.82
9	Argon	0.9	300	83.4	56.16	27.24	48.50
10	Argon	1.0	300	111	62.4	48.6	77.88

For the data obtained from the simulation, P-density, ΔP-density and RD-density curves are plotted with density as the horizontal coordinate and pressure as the vertical coordinate (Fig. 6-8).

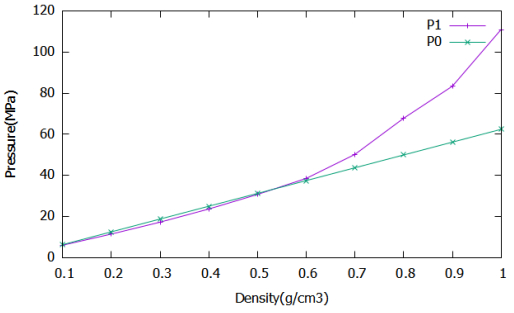

Figure 6. P-density curve at temperature of 300 K.

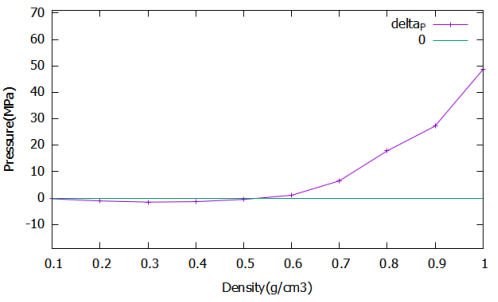

Figure 7. ΔP-density curve at temperature of 300 K.

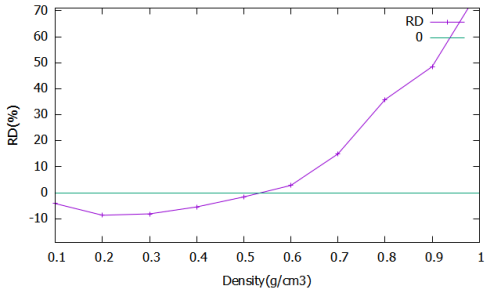

Figure 8. RD-density curve at temperature of 300 K.

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From the figures above, it can be seen that under the condition of temperature 300 K, the pressure in the system when the gas density is greater than 0.6 g/cm^3 has a large deviation from the theoretical prediction of the formula, so it can be initially judged that the ideal gas equation of state is basically applicable at the temperature of 300K and the gas density of 0.1-0.6 g/cm^3, and it is not applicable at the density of greater than 0.6 g/cm^3.

3. Modification of the equation

Based on the findings obtained from the preceding simulation results and further data processing, it is shown that the ideal gas equation of state exhibits greater applicability at lower gas densities. Conversely, for gases characterized by higher densities, significant deviations between the actual values and the predictions derived from the ideal gas equation of state are observed. The empirical equation for gases applicable under high density settings is obtained by parametrically correcting the ideal gas equation of state using data and statistical approaches, as indicated by the molecular simulation results.

3.1. Molecular simulation

Molecular simulations were first performed to obtain sufficient data, setting the temperature at 300 K and the density between 0.5 and 1.0 g/cm^3 at intervals of 0.01 g/cm^3, together with the data obtained in the previous steps (Table 6).

Table 6. Simulated data at 0.1-0.99 g/cm^3 for non-linear regression.

Serial number	ρ(g/cm^3)	P_1(MPa)	Serial number	ρ(g/cm^3)	P_1(MPa)
1	0.1	5.98	28	0.73	50
2	0.2	11.4	29	0.74	56
3	0.3	17.2	30	0.75	53.8
4	0.4	23.6	31	0.76	54.7
5	0.5	30.7	32	0.77	63.3
6	0.51	29.8	33	0.78	62.1
7	0.52	31.9	34	0.79	58.8
8	0.53	31.8	35	0.8	67.8
9	0.54	32	36	0.81	67.5
10	0.55	37	37	0.82	56
11	0.56	38.9	38	0.83	75.9
12	0.57	40.2	39	0.84	62.7
13	0.58	38	40	0.85	72.9
14	0.59	36.4	41	0.86	71.8
15	0.6	38.5	42	0.87	76.8
16	0.61	40.1	43	0.88	81.8
17	0.62	42.6	44	0.89	83.8
18	0.63	44.5	45	0.9	83.4
19	0.64	45.5	46	0.91	78.8
20	0.65	41.2	47	0.92	86.6
21	0.66	40.6	48	0.93	86.3
22	0.67	46.5	49	0.94	93.2
23	0.68	47	50	0.95	101
24	0.69	49.7	51	0.96	94.8
25	0.7	50.2	52	0.97	95.7
26	0.71	51.4	53	0.98	108
27	0.72	50	54	0.99	104

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3.2. Non-linear regression

Polynomial regression was used and suitable correction terms were added to create a new model for regression and also to compare the accuracy of the regression results. After several attempts, the results and parameters are as follows (Table 7, Fig. 9):

$$y = \alpha x + bx^6$$

Table 7. Regression Parameters.

Parameters	Parameter Values	Asymptotic Standard Error	Relative Standard Error
a	62.1858	±1.083	1.741%
b	48.6562	±2.074	4.262%

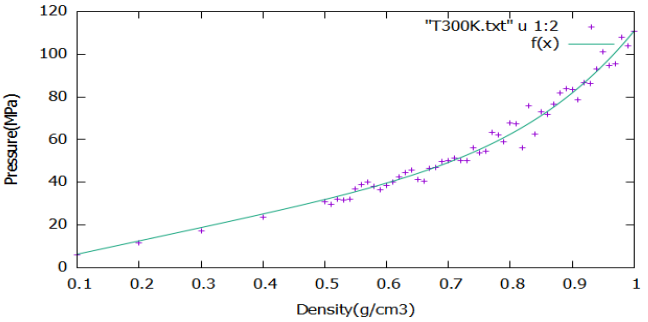

Figure 9. Polynomial regression.

The model regression results are good, from which we obtain the empirical gas equation applicable for Ar atoms in the case of high molecular density, which is applicable in the range of temperature 300K and gas density 0.1-1 g/cm^3:

$$P = \alpha\rho + b\rho^6$$

where P is the gas pressure, ρ is the gas density, and a and b are parameters determined from experimental data.

4. Conclusion

Following the successful validation of the molecular simulation method, it has been shown that the ideal gas equation of state is suitable for describing the behaviour of Ar atomic gas within the temperature range of 300-500K and the density range of 0.1-0.6 g/cm^3.

The application of the ideal gas equation of state is limited in situations characterised by high gas density, namely when the temperature exceeds 300K and the density surpasses 0.6g/cm3. The empirical gas equation was derived using statistical regression methods. From the equation's structure, it can be observed that the gas pressure is influenced by both the first and sixth power terms of its density. The empirical gas equation derived in this study is a concise representation of the statistical findings acquired from experimental data. However, the physical meaning of each parameter remains unclear, indicating that the equation is an empirical representation of the gas state. By conducting an analysis and deriving an empirical equation from a theoretical physical perspective, it is possible to elucidate the physical significance of the elements inside the empirical equation. This approach can significantly enhance the interpretability and correctness of the equation.

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