**Research** Article

# Refined Covolume Approach for Heavy Alkanes in Abel-Noble EOS at High Pressures

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# Abstract

A novel formulation was developed to accurately model volume behavior at very high pressures for heavy n-alkanes, based on excluded volume theory. This approach is crucial as several cubic equations of state become inadequate at pressures exceeding several thousand bars. The covolume formulation was applied to the Abel-Noble equation of state (EoS) for real gases to accurately model the specific volume of linear long-chain alkanes. It adjusts the compression limit volume of these heavy alkanes by tuning a small dimensionless parameter, epsilon ( $\epsilon$ ), which establishes a numerical relationship between pressure and excluded volume. At high pressure (from 50 MPa), the molar specific volumes of various aliphatic alkanes ( $C_nH_{2n+2}$ ) between 30 and 250 °C were carefully calculated. The proposed formulation was undoubtedly improved by comparing it with experimental data from many peer-reviewed studies, keeping a square error limit of 3% for heavy n-alkanes. Additionally, we notice that attempts to use the presented EoS for low-carbon number hydrocarbons seem unreliable until the fluid is set under very high pressure.

Keywords: Covolume; n-alkanes; high pressure; Abel-Noble EoS.

### 1. Introduction

The thermodynamic properties of hydrocarbons, primarily n-alkanes, which simply include carbon and hydrogen, at a certain pressure (P) and temperature (T) are ascertained using equations of state for fluids, which are also used to describe the phase behavior of those substances, thereby allowing the determination of the specific volume (v) at given P and T. In fact, most fluid PvT calculations in petroleum engineering cover reservoir models, well testing, pipeline flow calculations, separator design, and precise phase behavior predictions for various tertiary recovery procedures, such as gas injection, pyrolysis, or in situ combustion [1-2].

Designing engineering processes requires accurate experimental density measurements and trustworthy thermodynamic property estimates due to the rising activity in chemical and petroleum engineering. Moreover, oxidation reactions and hydrogen abstractions (H-abstraction) during the combustion of heavy n-alkanes play a key role in heat production. In petroleum refining, these mechanisms, particularly H-abstractions, are essential for breaking down heavy hydrocarbons into smaller, more useful molecules for fuel production.

Heavy alkane processing is generally carried out at high pressure and elevated temperatures. The auto-ignition and oxidation mechanisms of linear alkanes require a temperature range between 550 and 1100 K as mentioned by Biet et al. [3]. For example, the ignition delay time of such a hydrocarbon can be measured in a shock tube at temperatures above 1000 K, or predicted accurately using numerical simulations [4-5]. Although high temperatures are often preferred for the processing of long-chain alkanes due to their high thermal stability, certain conditions can benefit from lower temperatures as given by Bikas and Peters [6]. These include processes such as thermal and catalytic cracking (between 450°C and 750°C) or hydrocracking and hydrogenation (between 300°C and 450°C).

This paper aims to present a straightforward method for accurately analyzing the state of n-alkanes by correlating pressure with the excluded volume and investigating its effect on the specific volume. Using the main idea of Van

Der Waals, we can ignore repulsive forces under sufficiently high pressure that every material should undergo structural transformations towards denser and tighter atomic arrangements. Since these are input data for the aforementioned calculations, their accuracy is critical. Incorrect PvT properties lead to erroneous calculation results, so the calculation method used must be carefully selected [7]. We emphasize that aliphatic hydrocarbons, which lack double or triple bonds that are highly reactive in organic chemistry, are not entirely unreactive. While they do exhibit some reactivity, their generally low reactivity in most laboratory settings makes them a relatively stable but crucial component of organic chemistry.

### 2. Model Development

### 2.1. EoS Theory

Based on experimental observations and well-founded theoretical investigations, a wide range of equations of state (EoS) have been produced. As a result, an EoS has a wellestablished reputation for adaptability in computing pressure as a function of density and temperature. To characterize the behavior of fluids under high pressures and temperatures, various models (equations of state) have been developed to date. Indeed, the use of equations of state to characterize the P-v-T properties of materials began in 1873 with van der Waals' introduction of his groundbreaking equation. The EoS Virial, a power series formulation of the fluid compressibility factor density, was proposed in 1901 [8]. Despite being proposed as an empirical form, the Virial equation was eventually proved to be derived from statistical mechanics. This equation's fundamental weakness is that it cannot describe multiphase events.

Both the Redlich-Kwong and Peng-Robinson EoSs offered highly successful equations about fifty years later as mentioned by Liu et al. for compressible alkanes [9]. In fact, cubic equations are most usefully applied at high-pressure levels that cannot exceed the supercritical zone [10]. These cubic EoSs are commonly utilized to predict hydrocarbon phase behavior and volumetric features [11]. In the compressible state, estimating the thermodynamic characteristics of nonpolar fluids such as aliphatic alkanes and their mixes was simple and reasonably accurate. At pressures of several hundred bars, cubic equations such as Peng-Robinson or Redlich-Kwong remain relatively reliable, particularly for gases at moderate temperatures. However, their accuracy decreases when complex phenomena, such as liquefaction or phase formation, occur. These equations often struggle to accurately represent such phenomena in condensed phases (liquid or supercritical), where molecular density is extremely high [4]. Furthermore, structural modifications of molecules in these dense phases are not always adequately accounted for in the formulations of cubic equations, which can lead to inaccurate predictions of alkane behavior under high-pressure conditions.

Additionally, we see in the literature that several formulations of PvT are based on the scaled-particle theory for hard spheres for n-alkanes. Therefore, Vega et al. highlighted several applications for this form of EoS at a low-pressure level [12]. The equation of state for hard spheres is defined using a form factor, also known as a structural factor, which depends on the hard sphere's diameter. Recently, Eslami et al. provided a modified perturbed hard-sphere-chain equation of state that has been used to calculate fluid PvT properties, specifically for C1–C20, where predictions are more accurate than those of the original perturbed hard-sphere-chain equation of state without modification [13].

In general, an EoS, described in these models summarizes two major molecular effects (agitation and repulsion effects) in a simpler formulation. The corresponding parameters are derived using the experimental saturation findings as reference data. Furthermore, a basic EoS model for hydrocarbons has proven to be a useful tool for engineering applications such as petrochemicals. The issue of using a cubic equation technique to determine largescale correlations, on the other hand, remains an open question. It is especially challenging to transition from the scaled equation of state used in the critical area to practical and well-understood analytical forms, or when the fluid (heavy n-alkane) is in the weakly compressible liquid state.

We cited the empirical model of Orwoll and Flory, which expressed the density of n-alkanes entirely as a function of temperature [14]. We also highlighted other empirical equations used to calculate the densities of n-alkanes and their mixtures, employing a modified version of the Tait equation of state, as reported by Bamgbade et al., whose PvT relationship was valid only at low and moderate pressures [15].

Additionally, the Abel-Noble equation is a simple yet effective tool for modeling the behavior of real fluids under moderate conditions. Its mathematical simplicity and low requirements for adjustable parameters make it practical in many situations. By adding simple correlations, this equation can be kept in its fully analytical form. Studies have evaluated its use with low-carbon-number alkanes under high pressure, often modeling hydrocarbons by eliminating the attraction energy term with minimal precision loss [16].

It is discovered that its deviations from published experimental data at a wide range of pressures and moderate temperatures are slightly higher than those calculated for the same compounds using complicated EoS. Using only experimental data points at reduced pressures of less than 2 for parameter fitting, as is common in most commercial chemical processes, results in smaller deviations from experimental values. While the Noble-Abel equation allows for quick and reasonably accurate specific volume calculations at high densities and temperatures, more developed models are needed for extreme pressure and temperature conditions.

# 2.2 Covolume Models

Determining the covolume for the equation of state calculations, as proposed by Abel-Noble, is useful when combined with van der Waals theory. Arteca explained that covolume, typically considered constant in cubic equations, represented the molar volume of a liquid near its melting point, including both the excluded molecular volume and inter-molecular voids [17]. It reflects the fluid's inability to be compressed indefinitely at a constant temperature, with volume approaching an incompressible threshold as pressure increases. Studies by Höhne and Blankenhorn and Machado et al. examined the behavior of n-alkane mixtures under high pressures, addressing issues like solid-to-solid transitions that can obstruct process lines [18-19].

Because they are made of a structured long chain, aliphatic n-alkanes have a distinct polarity characteristic. Alkanes are insoluble in aqueous solutions because their molecules are nonpolar and cannot interact with water molecules to disperse. Molecules with similar structures, even non-polar ones, can interact and scatter into one another. Alkanes, for instance, are excellent solvents for each other and for organic compounds in general. As the system gets closer to the volume limit of near incompressibility, at extremely high pressures, the covolume stabilizes at a constant value.

Based on the molecular structure and carbon number of the given n-alkane, we used two different formulations of the covolume required for the EoS calculation in this analysis. The molar covolume is calculated using the Van Der Waals model Eq. (1), the Redlich Kowng model Eq. (2), and the Kumar et al. model Eq. (3), which is only valid for n-alkanes [20]. These formulations will be compared to the new covolume correlation used in the current study.

Firstly, the well-known Van Der Waals covolume model is as follows, where  $T_c$  and  $P_c$  as shown in table 1, denote the critical temperature and pressure of the given pure compound, respectively:

$$b_{vdw} = \frac{RT_C}{8P_C} \tag{1}$$

Therefore, the corresponding expression for the Redlich-Kwong covolume formula is written as follows:

$$b_{rk} = 0,08664 \frac{{}^{RT}{_{C}}}{{}^{P}{_{C}}} \tag{2}$$

For heavy alkanes, most studies highlighted the limitations of cubic equations, particularly at high pressures. Kumar et al. addressed this issue by introducing a relationship between covolume and molar mass [20]. They calculated the covolume *b* values for n-alkanes as follows, where  $M_w$  is the molar weight of the considered n-alkane:

$$b_k = -14.69921 + 0.36977 \, M_w - 9.12089 \, M_w^2 \, .10^{-5} \tag{3}$$

Table 1. Physical Properties of some n-Alkanes.

n-Alkanes	Carbon	Hydrogen	M <sub>w</sub>	Critical	Critical
	number	Number	(g/mol)	Temperature	Pressure
	N <sub>C</sub>	$N_h$		(K)	(bar)
n-Methane	1	4	16.04	190,5	46,0
n-Propane	3	8	44.09	369,8	42,5
n-butane	4	10	58.12	425,1	37,9
n-pentane	5	12	72.15	407,8	36,4
n-hexane	6	14	86.17	469,7	33,7
n-heptane	7	16	100.20	461,0	34,1
n-octane	8	18	114.22	433,8	32,0
n-nonane	9	20	128.25	507,6	30,2
n-decane	10	22	142.28	497,5	30,1
n-undecane	11	24	156.30	504,4	31,2
n-dodecane	12	26	170.33	488,7	30,8
n-tridecane	13	28	184.35	499,8	31,3
n-tetradecane	14	30	198.38	540,2	27,4
n-heptadecane	17	36	240.46	540,5	28,9
n-eicosane	20	42	282.54	519,7	27,4
n-triacontane	30	62	422.80	553,5	25,6
n-tetracontane	40	82	563.06	567,8	28,7
n-pentacontane	50	102	703.32	617,7	21,1

The primary motivation for this study arises from analyzing molar-specific volume data obtained from experiments at various pressures and temperatures. The covolume is modeled as an exponential function that varies with pressure up to very high values. While the concept of covolume as a state-dependent parameter is not novel-Baibuz et al. previously noted its dependence on very high temperatures for real fluids-the current work proposes a new formulation of covolume for heavy alkanes under extreme pressures [21]. Also, we can underline the work of Chiapolino et al. who have taken the covolume as a function of the specific volume for liquid-gas systems far from the critical point [22]. By applying the Abel-Noble EoS and comparing the results with experimental data and Handbook values, this approach aims to refine the accuracy of the P-v-T relationship for these substances [23]. The Abel-Noble equation is a relatively simple yet effective approach to describe the behavior of real fluids under moderate conditions. Its mathematical simplicity and low requirements for adjustable parameters make it a practical tool in many situations.

In reality, under extremely high pressures, heavy alkanes approach a compressibility limit where their behavior shifts from what is typically expected. Instead of simply experiencing a uniform reduction in volume, the long-chain alkanes undergo a significant reorganization. The pressure causes these chains to become increasingly compact and aligned, leading to a more constrained arrangement of the molecules. At such high pressures, the concept of volume as a simple measure becomes inadequate. Instead, the behavior of these alkanes must be understood in terms of covolume the space that the molecules and their interactions effectively occupy. The chains don't just compress but adapt to a new molecular configuration where their movement is severely restricted.

This calls for a refined model where covolume varies with pressure to accurately reflect the constrained nature of the alkanes' long chains. By developing a model that accounts for this pressure-dependent behavior, we can better capture the complex interactions and spatial arrangements of heavy alkanes under extreme conditions. Such a model provides a more precise description of their properties, accommodating the unique effects of high-pressure environments on their molecular structure.

#### 2.3 Sources of Experimental Data

Our research only looks at the volume measurements of pure alkanes using techniques that have been published lately or in the last several decades.

Table 2. Published data of n-Alkanes density at different

runges of pressure and temperature.						
n-Alkanes	Temperature	Pressure	Year and			
n / manes	range (°C)	range (MPa)	ref.			
n methane	-182 - 327	< 100	(1988) [24]			
II-IIIetilalle	-183 - 327	< 200	(1987) [25]			
n propana	-187.6 - 327	< 100	(1987) [25]			
n-propane	-188 - 427	< 70	(1982) [26]			
	-138 - 327	< 70	(1987) [25]			
n-butane	50 - 170	13-69	(1992) [27]			
	25 - 175	< 30	(2015) [28]			
	50 - 150	7 - 241	(2000) [29]			
n nontano	75 - 150	8.1 - 65	(1992) [27]			
n-pentane	52.7 - 247.3	1.8 - 275.5	(2010) [9]			
	-178 - 613	< 300	(2004) [30]			
n havana	38 - 238	0.7 - 66.2	(1954) [31]			
II-IICXAIIC	40 - 175	0.2 - 65	(1992) [27]			
n-heptane	30 - 300	5- 500	(1964) [32]			
	25 - 200	0.1- 202	(2009) [33]			
n-octane	25 - 75	0.1 - 480	(1982) [34]			
	48.7-150.2	14.3-276.9	(2010) [9]			
n-nonane	30 - 300	5-500	(1964) [32]			
	25 - 100	0.1 - 192	(2009) [33]			
n-decane	25 - 100	.0.1 - 420	(1982) [34]			
	51.3 - 247	14.6 - 274.5	(2010) -[9]			
n-undecane	30 - 300	5- 500	(1964) [32]			
n dadaaana	25 - 300	0.1-81.1	(2004) [33]			
n-dodecane	293 - 433	0.1 - 140	(2003) [35]			
n-tridecane	30 - 300	5 - 500	(1964) [32]			
n-tetradecane	23-60	0.1-10	(2013) [36]			
n-heptadecane	50-300	5 - 500	(1964) [32]			
n-eicosane	100-300	5 - 500	(1964) [32]			
n-triacontane	150-300	5 -500	(1964) [32]			
n-tetracontane	150-300	5 - 500	(1964) [32]			
n-Octadecane	50-300	0.1-41.3	(2004) [33]			

As a result, specific molar volumes are calculated using data from linear alkane density and volume at various temperatures and pressure ranges (from 50 to 300 MPa). On the other hand, Lindberg et al. used pure chemicals like n-propane and n-heptane to quantify density up to a temperature of 473 K at low pressures [11]. The behavior of n-alkanes is somewhat compressible in these conditions, and covolume takes a minor role.

# 3. Results and Discussion

# 3.1 Model Describing

The presented EoS for heavy hydrocarbons at high pressure might be satisfying for many engineering applications. In fact, this EoS may be effectively included in thermochemical codes to resolve shock tube problems when a sudden, and strong temperature shift occurs, such as in the case of shock tube breakdown of hydrocarbons [5]. Using the equation of state, these algorithms concurrently solve for the state surfaces and the chemical byproducts composition such as n-alkanes. Thus, as long as the equations of state correctly characterize pure and mixed chemicals at various temperature and pressure ranges, it is simple to predict operational parameters throughout a transformation process.

$$b = \frac{M_w \varepsilon^2}{K(1+\varepsilon)} \left( 1 - e^{-\frac{\varepsilon P}{P_0}} \right) \tag{4}$$

The use of very small exponents ( $\varepsilon$ ) is often chosen in contexts where subtle modifications to a quantity or function are desired, without significantly altering the overall behavior of the target function. In this context, the exponent epsilon has a moderate effect on the function  $b(M_{W}, P)$ , gradually bringing it closer to a limiting value with an almost imperceptible impact. The smaller the exponent epsilon, the more gradual and discrete the effect becomes. This pressure-dependent form illustrates how pure compounds tend to reach the volume limit under very high pressures. This method allows for the adjustment of experimental density data across a wide range of n-alkanes. Here, K represents a dimensional constant (K=8.0), and P<sub>0</sub> is a reference pressure, such as atmospheric pressure. The Abel-Noble equation of state (EoS) can be expressed as follows:

$$v = \frac{1}{M_W} \left( \frac{RT}{P} + b \right) \tag{5}$$

where the gas-specific volume. The covolume b compensates for the finite volume occupied by the gas molecules and epsilon an arbitrarily small dimensionless value as  $\varepsilon$ =0.01.

#### **3.2 Effect of Epsilon**

Several n-alkanes were used to evaluate the proposed formulation in equations Eq. (4) and Eq. (5). Figure 1 illustrates the application of the proposed covolume for n-heptane and n-eicosane. At pressures ranging from 1 MPa to 300 MPa and a temperature of 100 °C, the specific volume of n-heptane was calculated, showing good agreement with the epsilon values (0.01, 0.005) presented in Figure 1(a). The analysis reveals that a minimal effect is observed when the epsilon parameter doubles, a principle applicable to the measurement of the specific volume of n-alkanes over a wide range of temperatures and under high pressures.

This study also compares the calculated specific volume data at (P, T) for n-eicosane with existing experimental results, using different epsilon values (0.01, 0.002, 0.005), as shown in Figure 1(b). Comparing these values highlights the refined effect of the exponents, with their impact remaining marginal in the estimation of specific molar volumes, particularly when these volumes deviate slightly from a target limiting value. The  $\varepsilon$  effect is often observed in chemical reactions or physical processes where small accumulated variations, such as radioactive decay, produce progressive but subtle effects over time.



Figure 1. Effect of  $\varepsilon$  value on the specific volume for both n-heptane (a) and n-eicosane (b) at 100°C.

### 3.3 Effect of Pressure on Covolume

The covolume parameter has different behavior under the given operating conditions than the bulk of preceding publications, which only provide a single temperature dependence that does not also satisfy the very high-pressure domain. This behavior has been recognized in the literature. The covolume parameter b is given a new pressuredependent function to prevent thermodynamic inconsistencies at high pressure.



*Figure 2. Effect on pressure on the covolume calculated with Eq.(4).* 

The proposed model shows that the covolume varies with carbon number as pressure gradually increases to thousands of bars, as illustrated in Figure 2, where the covolume is plotted as a function of the carbon number using equation (4). Even under extremely high pressure, the behavior remains exponential and reaches a constant value. For a given hydrocarbon, the covolume remains stable under high pressure. In this case, the curves for 300 MPa (green) and 500 MPa (\*asterisk) are virtually superimposed. When the relation is sufficiently smoothed, it yields satisfactory results compared to the one published by Kumar (Figure 3). In contrast, for the VDW and RK approaches, the covolume estimate remains somewhat imprecise.



Figure 3. Comparison with covolume correlation of Kumar et al. and those of Van Der Waals and Redlich-Kowng.

We analyzed the correlation between this work at high pressure and that determined from relation Eq. (3) given by Kumar et al., as well as the covolume b in VDW EoS, Eq. (1) and RK EoS Eq. (2). In reality, the covolume curves associated with the suggested techniques exhibit exponential behavior and trend to a constant value as pressure is significantly increased. Additionally, compared to the covolume produced by the current study and supported by Kumar's relation, the link providing the covolume from VDW theory tends to produce a lesser value. In fact, Suceska et al. demonstrate that this influence is related to nonspherical molecules because rotational motion is constrained at high pressures, which emphasizes the current relationship between the covolume and working pressure [37]. Thus, the current equation offers a good and precise correlation for the covolume of heavy aliphatic n-alkanes.

#### 3.4 Specific Volume Calculation for Several n-alkanes

At different temperatures and pressures, the PvT of aliphatic n-alkanes (C1-C50) is estimated using the proposed Abel-Noble EoS-based equation; see Table 2. The experimental data presented here was chosen because it gives precise volumes of both light and heavy n-alkanes at pressures up to 3000 bar. In practice, the volumetric properties of n-alkanes (C1-C50), typical examples of nonpolar hydrocarbons, were predicted using the modified Abel-Noble model. In this study, we compared our model to the exact aliphatic n-alkane volumes reported in the literature. To predict the density at higher pressures, only the temperature and molecular weight were employed as input variables. When all necessary experimental data were known, the epsilon term was frequently considered to be a minor constant. Otherwise, a squared average error threshold was used to compare the outcomes to those discussed in the literature.

The specific volume of several pure aliphatic n-alkanes over the high-pressure domain has barely shifted, according to the modified Abel-Noble model. However, even with a specific EoS that is only relevant at low pressure, the density of compressed liquids containing aliphatic alkanes may be predicted with great accuracy [38]. The new study enhances agreement with liquid densities by more precisely characterizing behavior up to 300 MPa and beyond and incorporating the pressure-dependent b into the offered EoS.







Figures 4. Comparison of experimental and simulated specific volume of listed aliphatic n-alkanes (table 1.) Straight lines depict simulated values through the equation Abel-Noble EoS) and red circles represent experimental data for the considered n-alkane.

Except for n-eicosane and n-heptadecane, which were tested at 250°C, figure 4 compares the specific volumes of the various n-alkanes mentioned in Table 1 were measured at 100 °C, at pressures ranging from a few bars to 300MPa. Three locations that stand out in the majority of the images demonstrate remarkable agreement between the model's (solid line) predictions at high pressure and the data provided in Table 2.

Heavy alkanes, due to their larger molecular size, experience significantly amplified molecular compression

effects under high pressures. Typically, the model's validity range is 50 to 300 MPa. Other calculations carried out at various temperatures (50°C, 250°C) with a more precise agreement demonstrate the same tendency. If the n-alkane is heavier, or has a higher carbon number, in the second computation zone, which involves moderate pressures between 100 and 500 bars, the agreement is demonstrated. Our model completely diverges in the final computational region, which is connected to low pressures, where the  $C_nH_{2n+2}$  is not always in a fluid condition. For instance, the cases of methane and heptane are presented to illustrate the limitations of the model's applicability.

The modified Abel-Noble EoS modeling specific volumes (in this case, n-triacontane) are reasonably accurate at high pressures, as shown in Figure 5 (up to 50 MPa). The modeling curves display identical exponential behavior and do not cross one another for a given temperature and pressure, indicating thermodynamic consistency. It should be emphasized that all parameter values of the study's component sections are fixed at 0.01, and no attempt is made to alter them as the inquiry develops. Future work will focus on making the optimal value of this little constant even better.

Furthermore, because it propagates in repulsive and chain terms, the pressure-dependent b enables the model to get excellent findings for liquid density. This method is more accurate than cubic EoS in a variety of ways when simulating the precise volume or density for a high-pressure range for a subset of n-alkanes. This equation may also determine the thermodynamic properties of a particular n-alkane with accuracy without the use of a hard-sphere approach or a complicated fluid state description, and it does so without relying on the attracting and repelling components from the traditional cubic EoS. This makes it simpler to write and faster to implement than chemical engineering.



Figure 5. Isotherms of n-triacontane calculated through the modified Abel-Noble EoS ( $\varepsilon$ =0.01).

However, the covolume Eq. (4) presented in this work has been compared to the standard representation of the Abel-Noble equation for n-heptadecane at room temperature  $(30^{\circ}C)$ . Here the pressure was varied from few bars to 3000 bars. The proposed equation accurately reproduces experimental measurements of the specific volume at very high pressure; however the Abel-Noble model equation generates extremely low values that are far from reality, figure 6.



Figure 6. Comparison of Isotherm (30°C) profile of n-heptadecane calculated through Abel-Noble EoS and the presented EoS ( $\varepsilon$ =0.01).

#### 3.5 Root Mean Square Relative Error Calculation

The mean relative error for the N data points serves as a reference for the EoS prediction's accuracy. The equation is validated in reality by comparing the estimated values to the experimental results using average deviation methodologies. The following are some uses for percent of the root mean square relative error (RMSRE). It was used to evaluate the performance of the model in percent:

$$\% \text{RMSRE} = \sqrt{\frac{1}{N} \sum_{k=1}^{k=N} \left(\frac{v_{exp} - v_{cal}}{v_{exp}}\right)^2}$$
(6)

Figure (7) presents the Root Mean Square Relative Mean Error (RMSRME) for the alkanes studied specifically methane (C1) and propane (C3), alongside heavier alkanes ranging from heptane (C7) to tetracontane (C40). Here, RMSRE is used to illustrate how the covolume formula in Eq. (4) can be used with Abel-Noble EoS to calculate  $v_{cal}$  for heavy aliphatic n-alkanes under high pressure. N is the total number of measurements at each temperature, and  $v_{exp}$  is based on data from the literature. The data indicate a significant error in the predictions for light alkanes (C1 and C3), where the model demonstrates considerable deviations from experimental results. This substantial error highlights the model's unsuitability for accurately capturing the thermophysical properties of light alkanes, likely due to the dominance of gaseous phase interactions and the reduced molecular complexity of smaller alkanes.

Conversely, the error becomes acceptable for heavier alkanes (C7-C40). This indicates that the model is better equipped to handle the interactions and phase behavior associated with larger molecular structures. Heavier alkanes exhibit more complex intermolecular interactions, including van der Waals forces and enhanced molecular compression effects under high-pressure conditions, which the model appears to capture more effectively.

The results confirm the model's applicability and reliability within the range of heavier alkanes. This behavior is likely due to the reduced influence of phenomena like gasphase behavior and liquefaction irregularities, which are more pronounced in light alkanes. Additionally, the denser molecular packing and more predictable structural properties of heavier alkanes may align better with the assumptions underlying the model. Thus, Figure (7) underscores the importance of carefully considering the molecular size and weight range when applying the model to alkanes, ensuring its use is restricted to the domain where its predictions remain valid.



Figure 7. Root mean square relative error from the computation specific volumes for various n-alkanes.

### 4. Conclusions

This study has enhanced our comprehension of the behavior of aliphatic n-alkanes under high pressure through the use of EoS modeling. To study a new generation equation of state that is created using a numerical approach, the research evaluates the absolute deviation technique. A modified Abel-Noble EoS is employed in this work to accurately reproduce the density of pure aliphatic n-alkanes behavior over a wide pressure range at a moderate temperature. The model uses the classic Abel-Noble model to demonstrate the non-ideality of the state by using the covolume (b) as a function of pressure.

The epsilon term has allowed the model to reliably predict the volume of the (CnH2n+2) throughout a wide variety of high-pressure conditions (from 50 to 300 MPa). This is comparable to the capabilities of actual fluid models.

### Nomenclature

- *b* Covolume or excluded volume (*ml/mol*)
- *N<sub>c</sub>* Carbon number of aliphatic alkane
- $P_0$  Ambient pressure (*MPa*)
- $\varepsilon$  Tiny numerical adjustable parameter
- $T_c$  Critical temperature (K)
- $P_c$  Critical pressure (*MPa*)
- $M_{\rm w}$  Molar mass (g/mol)
- *N* Number of data points
- *P* Pressure (*MPa*)
- *R* Gas constant (J/(K mol))
- T Temperature (K)
- *v* Specific volume (ml/g)

# Abbreviations

EoS Equatio	on of state
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- VDW Van Der Waals
- RK Redlich Kwong

# **References:**

 M. Mohsen-Nia, "A modified MMM EOS for highpressure PVT calculations of heavy hydrocarbons," *Journal of Petroleum Science and Engineering*, vol. 113, pp. 97–103, Jan. 2014, doi: 10.1016/j.petrol.2013.12.008.

- [2] J. C. de Hemptine, P. Mougin, A. Barreau, L. Ruffine, S. Tamouza, and R. Inchekel, "Application to Petroleum Engineering of Statistical Thermodynamics – Based Equations of State," *Oil & Gas Science and Technology - Rev. IFP*, vol. 61, no. 3, pp. 363–386, May 2006, doi: 10.2516/ogst:2006039a.
- [3] J. Biet, M. H. Hakka, V. Warth, P.-A. Glaude, and F. Battin-Leclerc, "Experimental and Modeling Study of the Low-Temperature Oxidation of Large Alkanes," *Energy & Fuels*, vol. 22, no. 4, pp. 2258–2269, May 2008, doi: 10.1021/ef8000746.
- [4] A. B. Moussa and H. Ksibi, "Numerical Simulation of a One-Dimensional Shock Tube Problem at Supercritical Fluid Conditions," *International Journal* of Fluid Mechanics Research, vol. 35, no. 1, pp. 38–50, Jan. 2008, doi:10.1615/interjfluidmechres.v35.i1.30.
- [5] H. Hachoum and H. Ksibi, "On the Generation of an Intense Temperature Gradient Through a Modified Shock Tube Hydrodynamics for a Possible Continuous Sterilization Process," *Strojnícky časopis/Journal of Mechanical Engineering*, vol. 72, no. 2, pp. 81–92, Nov. 2022, doi: 10.2478/scjme-2022-0018.
- [6] G. Bikas and N. Peters, "Kinetic modelling of n-decane combustion and autoignition," *Combustion and Flame*, vol. 126, no. 1–2, pp. 1456–1475, Jul. 2001, doi: 10.1016/s0010-2180(01)00254-1.
- [7] A. I. Rusanov, "Equation of state theory based on excluded volume," *The Journal of Chemical Physics*, vol. 118, no. 22, pp. 10157–10163, May 2003, doi: 10.1063/1.1572455.
- [8] G. M. Kontogeorgis, R. Privat, and J.-N. Jaubert, "Taking Another Look at the van der Waals Equation of State–Almost 150 Years Later," *Journal of Chemical & Engineering Data*, vol. 64, no. 11, pp. 4619–4637, Aug. 2019, doi: 10.1021/acs.jced.9b00264.
- [9] K. Liu, Y. Wu, M. A. McHugh, Hseen Baled, R. M. Enick, and B. D. Morreale, "Equation of state modeling of high-pressure, high-temperature hydrocarbon density data," *The Journal of Supercritical Fluids*, vol. 55, no. 2, pp. 701–711, Dec. 2010, doi: 10.1016/j.supflu.2010.10.004.
- [10] H. Ksibi, "The Solvent-Solute Interaction in Supercritical Solution at Equilibrium: Modeling and Related Industrial Applications," *International Journal* of Thermodynamics, vol. 7, no. 3, pp. 131–140, Sep. 2004, doi: 10.5541/ijot.1034000134.
- [11] G. E. Lindberg, J. L. Baker, J. Hanley, W. M. Grundy, and C. King, "Density, Enthalpy of Vaporization and Local Structure of Neat N-Alkane Liquids," *Liquids*, vol. 1, no. 1, pp. 47–59, Dec. 2021, doi: 10.3390/liquids1010004.
- [12] C. Vega, L. G. MacDowell, and P. Padilla, "Equation of state for hard n-alkane models: Long chains," *The Journal of Chemical Physics*, vol. 104, no. 2, pp. 701– 713, Jan. 1996, doi: 10.1063/1.470867.
- [13] H. Eslami, "A perturbed hard-sphere-chain equation of state: prediction from critical point constants," *Fluid Phase Equilibria*, vol. 216, no. 1, pp. 21–26, Feb. 2004, doi: 10.1016/j.fluid.2003.09.002.

- [14] R. A. Orwoll and P. J. Flory, "Equation- of-state parameters for normal alkanes. Correlation with chain length," *Journal of the American Chemical Society*, vol. 89, no. 26, pp. 6814–6822, Dec. 1967, doi: 10.1021/ja01002a002.
- [15] B. A. Bamgbade et al., "Measurements and modeling of high-temperature, high-pressure density for binary mixtures of propane with n-decane and propane with neicosane," *The Journal of Chemical Thermodynamics*, vol. 84, pp. 108–117, May 2015, doi: 10.1016/j.jct.2014.12.015.
- [16] P. Longwell, J. Olin, and B. Sage, "Covolumes for a Number of Common Gases.," Industrial & Engineering Chemistry Chemical & Engineering Data Series, vol. 3, no. 2, pp. 175–180, Oct. 1958, doi: 10.1021/i460004a001.
- [17] G. A. Arteca, "Interpretation of covolume in an extension of the Redlich–Kwong equation of state for real gases," *Journal of Mathematical Chemistry*, vol. 61, no. 9, pp. 1967–1979, Aug. 2023, doi: 10.1007/s10910-023-01497-1.
- [18] G.W.H. Höhne and K. Blankenhorn, "High pressure DSC investigations on n-alkanes, n-alkane mixtures and polyethylene," *Thermochimica acta*, vol. 238, pp. 351– 370, Jun. 1994, doi: 10.1016/s0040-6031(94)85219-7.
- [19] J. J. B. Machado, Theo, E. Christian Ihmels, K. Fischer, and Jürgen Gmehling, "High pressure solid-solid and solid-liquid transition data for long chain alkanes," *The Journal of Chemical Thermodynamics*, vol. 40, no. 12, pp. 1632–1637, Jul. 2008, doi: 10.1016/j.jct.2008.07.017.
- [20] A. Kumar and R. Okuno, "Direct perturbation of the Peng–Robinson attraction and covolume parameters for reservoir fluid characterization," *Chemical Engineering Science*, vol. 127, pp. 293–309, May 2015, doi: 10.1016/j.ces.2015.01.032.
- [21] V. F. Baibuz, V. Yu. Zitserman, L. M. Golubushkin, and I. G. Malyshev, "The covolume and equation of state of high-temperature real gases," *Journal of Engineering Physics*, vol. 51, no. 2, pp. 955–956, Aug. 1986, doi: 10.1007/bf00871197.
- [22] A. Chiapolino and R. Saurel, "Extended Noble–Abel Stiffened-Gas Equation of State for Sub-and-Supercritical Liquid-Gas Systems Far from the Critical Point," *Fluids*, vol. 3, no. 3, p. 48, Jul. 2018, doi: 10.3390/fluids3030048.
- [23] M. J. Anselme, M. Gude, and A. S. Teja, "The critical temperatures and densities of the n-alkanes from pentane to octadecane," *Fluid Phase Equilibria*, vol. 57, no. 3, pp. 317–326, Jan. 1990, doi: 10.1016/0378-3812(90)85130-3.
- [24] D. G. Friend, J. F. Ely, and H. Ingham, "Thermophysical Properties of Methane," *Journal of Physical and Chemical Reference Data*, vol. 18, no. 2, pp. 583–638, Apr. 1989, doi: 10.1063/1.555828.
- [25] B. A. Younglove and J. F. Ely, "Thermophysical Properties of Fluids. II. Methane, Ethane, Propane, Isobutane, and Normal Butane," Journal of Physical and

Chemical Reference Data, vol. 16, no. 4, pp. 577–798, Oct. 1987, doi: 10.1063/1.555785.

- [26] R. D. Goodwin and W. M. Haynes, "Thermophysical properties of propane from 85 to 700 K at pressures to 70 MPa," OSTI ID: 6402039, Jan. 1982, doi: 10.6028/nbs.mono.170.
- [27] E. Kiran and Y. L. Sen, "High-pressure viscosity and density of n-alkanes," *International Journal of Thermophysics*, vol. 13, no. 3, pp. 411–442, May 1992, doi: 10.1007/bf00503880.
- [28] S. Glos, Reiner Kleinrahm, and W. Wagner, "Measurement of the (p,ρ,T) relation of propane, propylene, n-butane, and isobutane in the temperature range from (95 to 340) K at pressures up to 12 MPa using an accurate two-sinker densimeter," *The Journal* of Chemical Thermodynamics, vol. 36, no. 12, pp. 1037–1059, Dec. 2004, doi: 10.1016/j.jct.2004.07.017.
- [29] S. Herrmann and E. Vogel, "Viscosity and Density of Normal Butane Simultaneously Measured at Temperatures from (298 to 448) K and at Pressures up to 30 MPa Incorporating the Near-Critical Region," *Journal of Chemical & Engineering Data*, vol. 60, no. 12, pp. 3703–3720, Oct. 2015, doi: 10.1021/acs.jced.5b00654.
- [30] H.-S. Byun, T. P. DiNoia, and M. A. McHugh, "High-Pressure Densities of Ethane, Pentane, Pentane-d12, 25.5 wt Ethane in Pentane-d12, 2.4 wt Deuterated Poly(ethylene-co-butene) (PEB) in Ethane, 5.3 wt Hydrogenated PEB in Pentane, 5.1 wt Hydrogenated PEB in Pentane-d12, and 4.9 wt Hydrogenated PEB in Pentane-d12+ 23.1 wt Ethane," *Journal of Chemical & Engineering Data*, vol. 45, no. 5, pp. 810–814, Sep. 2000, doi: 10.1021/je990308+.
- [31] A. K. Doolittle, "Specific Volumes of n-Alkanes.," *Journal of Chemical & Engineering Data*, vol. 9, no. 2, pp. 275–279, Apr. 1964, doi: 10.1021/je60021a048.
- [32] D. R. Caudwell, M. Trusler, Velisa Vesovic, and W. A. Wakeham, "Viscosity and Density of Five Hydrocarbon Liquids at Pressures up to 200 MPa and Temperatures up to 473 K," *Journal of Chemical & Engineering Data*, vol. 54, no. 2, pp. 359–366, Feb. 2009, doi: 10.1021/je800417q.
- [33] J. H. Dymond, J. Robertson, and J.D Isdale, "(p, ρ, T) of some pure n-alkanes and binary mixtures of n-alkanes in the range 298 to 373 K and 0.1 to 500 MPa," *The Journal of Chemical Thermodynamics*, vol. 14, no. 1, pp. 51–59, Jan. 1982, doi: 10.1016/0021-9614(82)90123-9.
- [34] T. S. Khasanshin, A. P. Shchamialiou, and O. G. Poddubskij, "Thermodynamic Properties of Heavy n-Alkanes in the Liquid State: n-Dodecane," *International Journal of Thermophysics*, vol. 24, no. 5, pp. 1277–1289, Jan. 2003, doi: 10.1023/a:1026199017598.
- [35] M. Kariznovi, H. Nourozieh, J. G. James) Guan, and J. Abedi, "Measurement and modeling of density and viscosity for mixtures of Athabasca bitumen and heavy n-alkane," *Fuel*, vol. 112, pp. 83–95, Oct. 2013, doi: 10.1016/j.fuel.2013.04.071.

- [36] Vlastimil Růžička, M. Zábranský, and V. Majer, "Heat capacities of organic compounds in liquid state II. C1 to C18 n-alkanes," *Journal of Physical and Chemical Reference Data*, vol. 20, no. 2, pp. 405–444, Mar. 1991, doi: 10.1063/1.555883.
- [37] M. Suceska, H.-G. Ang, and H. Y. Serene Chan, "Study of the Effect of Covolumes in BKW Equation of State on Detonation Properties of CHNO Explosives," *Propellants, Explosives, Pyrotechnics*, vol. 38, no. 1, pp. 103–112, Nov. 2012, doi: 10.1002/prep.201100150.