

Obtaining the compressibility factor via intermolecular potentials without assuming pairwise additivity (The three dimensional Case)

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ABSTRACT

The focus here is to obtain the Compressibility Factor (CF) for pure fluids from a Configurational Integral (CI). In this direction, we came up with a formula from the (CI) which consistently gives the compressibility factor for a given intermolecular potential. From this formula we obtain the Compressibility Factor (CF) for a number of existing intermolecular potentials. The results here are compared with the Carnahan Sterling Equation of state (EOS) since it is one of the accepted EOS. There is a strong positive correlation between the results.

Keywords: Compressibility Factor, Fluids, Intermolecular Potentials, Pairwise Additive, Radial Distribution Function

I. INTRODUCTION

This work used a different approach; the compressibility factor is obtained from a configurational integral, which is good. The advantage here is that the (CI) creates an environment that paves the way to obtain expressions for the other thermodynamic variables. The compressibility factor also referred to as (Equation of State) has been obtained in a number of ways for more than a century. Van der Waal in 1873 came up with $\left(P + \frac{a}{V^2}\right)(V - b) = RT$.

Where a and b are constants. [2]

Other authors also gave similar contributions. Later the virial equation of state was introduced

$$Z = \frac{P}{kT\rho} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \dots \quad [3] \quad \text{here } B_2(T), B_3(T) \text{ etc. are constants}$$

In the late 1940's obtaining an equation of state (compressibility factor) using intermolecular potentials by assuming pair – wise additivity came into the picture [4 5 6].

An intermolecular potentials is pairwise additive if it can be expressed in the form

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \phi(|\mathbf{r}_i - \mathbf{r}_j|) \quad (\text{Note } |\mathbf{r}_i - \mathbf{r}_j| = r_{ij})$$

Now, due to Green

$$P = \rho kT - \frac{2\pi}{3} \rho^2 \int r_{12} \frac{\partial \phi(r_{12})}{\partial r_{12}} g(r_{12}) r_{12}^2 dr_{12} \quad (1)$$

Which simplifies to

$$\frac{P}{\rho kT} = 1 - \frac{2\pi\rho}{3kT} \int r \frac{\partial \phi(r)}{\partial r} g(r) r^2 dr$$

ρ is the number density

T is the temperature

P is the pressure

$\phi(r)$ is the intermolecular potential

Z is the compressibility Factor

$g(r)$ is the radial distribution function



r is the radial component of the position vector (the magnitude of displacement)

r_{12} is the average distance between particle 1 and particle 2

$$r_{12} = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}$$

$$\mathbf{r}_i = (x_i, y_i, z_i)$$

$$y = r_{12}$$

κ is Boltzmann's constant

Thus, Z and $g(r)$ (The radial distribution function) are connected through the relationship

$$Z = 1 - \frac{2\pi\rho}{3kT} \int r \frac{\partial\phi(r)}{\partial r} g(r)r^2 dr \quad (2)$$

The integral equation (2) is used to estimate Z and $g(r)$, from which, a barrage of equations of state (EOS) has been proposed. Equations of state obtained from equation (2) are considered Pairwise additive. To name a few, there are contributions from Reiss, Frisch and Lebowitz, [8], Ree and Hoover [9 10], Carnahan and Sterling [11], etc.

1.1 Statement of the Problem

In Statistical Mechanics, Thermodynamic variables are obtained from the Partition Function (PF) which was unavailable. As a result alternative methods to obtain the Compressibility Factor (CF) were proposed.

1.2 Research Objective

The objectives of this research are:

- (i) To come up with the configurational Integral in spherical coordinates
- (ii) To showcase the configurational Integral
- (iii) To use the configurational Integral to obtain the Compressibility Factor
- (iv) To obtain results in analytical, tabular or graphical forms.
- (v) To compare our result with other existing (EOS).

II. LITERATURE REVIEW

2.1 Theoretical Review

Statistical Mechanics studies fluids from their molecular properties. To achieve this, a partition function (PF) is required since from it, all the other Thermodynamic variables can be obtained. The configurational integral (CI) is key towards the derivation of the Partition Function (PF) since they are related. The intermolecular potential is needed in order to obtain the (CI). A number of intermolecular potentials have been proposed.

2.2 Empirical Review

In practice, a result obtained in an experiment might slightly vary with that from theory. The results obtained from experiments contribute towards the development of the theory. The (PF) and the (CI) were unavailable and so the research took an alternative approach to come up with expressions for a number of Thermodynamic variables. One such approach is to assume that the Intermolecular potential is pairwise additive.

III. METHODOLOGY

Mathematical formulae and Technics are used here. For Instance, the mathematical formulae are valid whenever $m \in \mathbb{Z}^+$ (m is a positive integer) and $n \in \mathbb{N}$ (n is a natural number). Here n is the order of integration. These formulae are useful in this study.

$$\int_a^y \cdots \int_a^y (y-a)^m dy_1 \cdots dy_n = \frac{m!}{(m+n)!} (y-a)^{m+n} \quad (3)$$

Now the following formulae are valid and are derived using trigonometry

$$(\sin \theta)^{2m} = 2^{-2m} \left[\binom{2m}{m} + 2 \sum_{r=1}^m (-1)^r \binom{2m}{m-r} \cos 2r\theta \right] \quad (4)$$

$$(\sin \theta)^{2m+1} = 2^{-2m} \left[\sum_{r=0}^m (-1)^{m-r} \binom{2m+1}{m-r} \sin(2r+1)\theta \right] \quad (5)$$



See for instance [1]

3.1 The Configurational Integral

The configurational integral [5 6 7]

$$Q_{NVT} = \int \exp(-\beta U(\vec{v})) d\vec{v}^N$$

$Q = Q_{NVT}$ is the configurational integral

(r, θ, ϕ) represents the spherical coordinates

Here $[\vec{v} = (v_1, v_2, \dots, v_N)$ while $d\vec{v}^N = dv_1 dv_2 \dots dv_N$ (v_i is the volume)

In terms of the three dimensional spherical coordinates $dv_i = r_i^2 \sin \theta_i dr_i d\theta_i d\phi_i$

Our Configurational Integral becomes

$$Q_{NVT} = Q_3 = \int e^{-\beta U(r, \theta, \phi)} \prod_{i=1}^N r_i^2 \sin \theta_i dr_i d\theta_i d\phi_i \quad (6)$$

$(r = r_1, \dots, r_N)$, $(\theta = \theta_1, \dots, \theta_N)$, $(\phi = \phi_1, \dots, \phi_N)$ and Q_3 is the configurational integral for the three dimensional case. We obtain the partition function as

$$Z_{pf} = \frac{1}{\Lambda^{3N} N!} Q_3 \quad (7)$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{\frac{1}{2}}$$

Z_{pf} is the partition function

Λ is the De Broglie Thermal Wave length

h is Planks constant

σ is the diameter of the molecule

N is the number of particles (it also refers to number of integrations)

In terms of N particles

$$Q = \int_0^\pi \dots \int_0^\pi d\phi_1 \dots d\phi_N \int_0^\pi \dots \int_0^\pi \sin^N \theta d\theta_1 \dots d\theta_N \int_\sigma^r \dots \int_\sigma^r e^{-U(r)} r^{2N} dr_1 \dots dr_N$$

At this stage, let $f(y) = y^{2N} e^{-U(y)}$ and so that

$$Q_3 = \int_0^\pi \dots \int_0^\pi d\phi_1 \dots d\phi_N \int_0^\pi \dots \int_0^\pi \sin^N \theta d\theta_1 \dots d\theta_N \int_a^y \dots \int_a^y f(y) dy_1 \dots dy_N$$

(here, n , y and a are variable substitutes, ($n = N$), ($y = r$) and ($\sigma = a$))

3.2 The use of Taylor Series

Sometimes direct integration with the nature of problems faced here may be challenging. Expressing $f(y)$ as a Taylor series expansion is helpful since equation (3) comes in handy. The key problems faced here are usually in the

$$\text{form } I(y) = \int_a^y \dots \int_a^y f(y) dy_1 \dots dy_n.$$

In order to use equation (3), the function $f(y)$ must be analytic, so that it can be expressed (or approximated) as a Taylor series about a .

$$\text{i.e. } f(y) = f(a) + (y-a)f'(a) + \frac{(y-a)^2}{2!} f''(a) + \dots + \frac{(y-a)^r}{r!} f^{(r)}(a) + \dots \quad (8)$$



Simply we say, $f(y) = \sum_{r=0}^{\infty} \frac{(y-a)^r}{r!} f^{(r)}(a)$. This expression can also be expressed as $f(y) = \sum_{r=0}^{\infty} a_r (y-a)^r$ where

$$a_r = \frac{f^{(r)}(a)}{r!} \quad [13]$$

This will enable us to obtain equations in the form

$$\begin{aligned} I(y) &= \int_a^y \cdots \int_a^y f(y) dy_1 \cdots dy_n = \int_a^y \cdots \int_a^y \sum_{r=0}^{\infty} \frac{(y-a)^r}{r!} f^{(r)}(a) dy_1 \cdots dy_n \\ &= \sum_{r=0}^{\infty} \int_a^y \cdots \int_a^y \frac{(y-a)^r}{r!} f^{(r)}(a) dy_1 \cdots dy_n \\ &= \sum_{r=0}^{\infty} \frac{r!}{(r+n)!} \frac{(y-a)^{r+n}}{r!} f^{(r)}(a) \quad \text{by equation (3)} \\ &= \sum_{r=0}^{\infty} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a) \end{aligned} \quad (9)$$

The pressure equation is given by

$$P = kT \left(\frac{\partial \ln Z_{pf}}{\partial V} \right)_{NT} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{NT}$$

$$\text{Let } I_n = \sum_{r=0}^{\infty} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a)$$

$$\text{Now since } \left(\frac{\partial \ln Q}{\partial V} \right)_{NT} = \left(\frac{\partial \ln I_n}{\partial V} \right)_{NT}$$

From this we deduce that [5],

$$P = kT \left(\frac{\partial \ln I_n}{\partial V} \right)_{NT}$$

$$\text{Thus } \left. \frac{\partial \ln Z_{pf}}{\partial V} \right|_{N,T} = \left. \frac{\partial \ln Z_{pf}}{\partial y} \right|_{N,T} \frac{dy}{dV} \Big|_{N,T} = \frac{I_n'}{I_n} \Big|_{N,T} \frac{dy}{dV} \Big|_{N,T} \quad (10)$$

$$V_3 \propto N \left(\frac{1}{6} \pi y^3 \right) \Rightarrow V_3 = \gamma \left(\frac{1}{6} \pi y^3 \right), \quad (\text{Where } \gamma \text{ is a constant}) \text{ Thus } \frac{dV_3}{dy} = \frac{\gamma}{2} \pi y^2$$

Here $y = r_{12}$

V_3 is the volume

$$\begin{aligned} P &= \frac{2\kappa T \sum_{r=0}^{\infty} \frac{(y-a)^{r+n-1}}{(r+n-1)!} f^{(r)}(a)}{\gamma \pi y^2 \sum_{r=0}^{\infty} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a)} \\ PV_3 &= \frac{y\kappa T \sum_{r=0}^{\infty} \frac{(y-a)^{r+n-1}}{(r+n-1)!} f^{(r)}(a)}{3 \sum_{r=0}^{\infty} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a)} \end{aligned}$$



$$\frac{PV_3}{nkT} = \frac{y \sum_{r=0}^{\infty} \frac{(y-a)^{r+n-1}}{(r+n-1)!} f^{(r)}(a)}{3n \sum_{r=0}^{\infty} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a)}$$

Thus

$$Z(y) = \frac{y \sum_{r=0}^{\infty} \frac{(y-a)^{r+n-1}}{(r+n-1)!} f^{(r)}(a)}{3n \sum_{r=0}^{\infty} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a)} \tag{11}$$

For optimal solution

$$Z(y) = \frac{y \sum_{r=0}^{2n} \frac{(y-a)^{r+n-1}}{(r+n-1)!} f^{(r)}(a)}{3n \sum_{r=0}^{2n} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a)} \tag{12}$$

This can also be written as

$$Z(y) = Z(y, n, a)$$

3.3 RELATIONSHIP BETWEEN y and η (the Scale Density)

The three dimensional case

Consider a $k \times k \times k$ cube which holds N particles. Assume each particle is fitted into a cube.

Volume of (a cube of side y) is y^3 . For a total of N such cubes, total volume = Ny^3

Without loss of generality,

$$\rho = \frac{N}{V} = \frac{N}{Ny^3} = \frac{1}{y^3} \tag{13}$$

((13) agrees with astrophysics results)

$$\eta_3 = \rho V_0 = \frac{N}{V} \frac{1}{6} \pi \sigma^3, \text{ which reduces to}$$

$$\eta_3 = \frac{N}{Ny^3} \frac{1}{6} \pi \sigma^3 = \frac{\pi}{6} \left(\frac{\sigma}{y} \right)^3 \tag{14}$$

IV. FINDINGS & DISCUSSION

4.1 The Hard Sphere

For the Hard Sphere potential (HSP)

$$\phi(y) = \begin{cases} 0 & y > \sigma \\ \infty & y < \sigma \end{cases}$$

Here σ is the diameter of the atom or molecule, while y is the average distance between two atoms or molecules

The configurational integral for the three dimensional hard sphere is given by

$$Q_3 = 2^{-2n} \int_0^\phi \int_0^\phi \dots \int_0^\phi d\phi_1 \dots d\phi_n \int_0^\theta \int_0^\theta \dots \int_0^\theta \sin^n \theta_1 d\theta_1 \dots d\theta_n \int_\sigma^r \int_\sigma^r \dots \int_\sigma^r r_1^{2n} dr_1 \dots dr_n \tag{15}$$

$$\text{Let } I(y) = \int_a^y \int_a^y \dots \int_a^y y^{2n} dy_1 \dots dy_n$$



For the Hard Sphere $f(y) = y^{2n}$

$$f^{(r)}(y) = (2n)(2n-1)(2n-2)\cdots(2n-r-1)y^{2n-r} = \frac{(2n)!}{(2n-r)!}y^{2n-r}$$

$$f^{(r)}(a) = \frac{(2n)!}{(2n-r)!}a^{2n-r}$$

So with the variable substitution $\sigma = a$

$$I = \sum_{r=0}^{2n} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a)$$

from equation (9)

$$\begin{aligned} I &= \int_a^y \cdots \int_a^y f(y) dy_1 \cdots dy_n = \sum_{r=0}^{2n} \frac{(y-a)^{r+n}}{(r+n)!} \frac{(2n)!}{(2n-r)!} a^{2n-r} \\ &= \frac{(2n)!}{(3n)!} (y-a)^n a^{2n} \sum_{r=0}^{2n} \binom{3n}{2n-r} \left(\frac{y-a}{a}\right)^r \end{aligned} \quad (16)$$

$$\int_0^\pi \int_0^\phi \cdots \int_0^\phi d\phi_1 \cdots d\phi_N = \frac{\pi^N}{N!} \quad (17)$$

$$\gamma_n = \int_0^\pi \int_0^\theta \cdots \int_0^\theta \sin^N \theta_1 d\theta_1 \cdots d\theta_N$$

$$Q = 2^{-2n} \frac{\pi^n}{n!} \gamma_n \frac{(2n)!}{(3n)!} (y-a)^n a^{2n} \sum_{k=0}^{2n} \binom{3n}{2n-k} \left(\frac{y-a}{a}\right)^k$$

In the event that n is even, say for instance $n = 2m$

$$\gamma_n = \int_0^\pi \int_0^{\theta_1} \cdots \int_0^{\theta_2} \sin^n \theta_1 d\theta_1 \cdots d\theta_n \cong 2^{-n} \frac{\pi^n}{n!} \binom{2m}{m}$$

Which gives

$$Q \cong \frac{2^{-n}}{(3n)!} \left(\frac{\pi}{2}\right)^{2n} \binom{2n}{n} \binom{2m}{m} (y-a)^n a^{2n} \sum_{k=0}^{2n} \binom{3n}{2n-k} \left(\frac{y-a}{a}\right)^k \quad (18)$$

see [1]

This expression was derived, based on the assumption that, n is even, i.e. $n = 2m$ and also $m \geq 10$

The formula [12] $\sum_{k=0}^{2n} \binom{3n}{2n-k} (q-1)^k = \sum_{k=0}^{2n} \binom{n-1+k}{n-1} (q)^{2n-k}$ is helpful to simplify (16) and (18)

4.2 The Compressibility Factor

From equation (12)

$$Z(y) = \frac{y \sum_{r=0}^{2n} \frac{(y-a)^{r+n-1}}{(r+n-1)!} f^{(r)}(a)}{3n \sum_{r=0}^{2n} \frac{(y-a)^{r+n}}{(r+n)!} f^{(r)}(a)}$$

$$\text{With } f(y) = y^{2n} \text{ and } f^{(r)}(a) = \frac{(2n)!}{(2n-r)!} a^{2n-r}$$

Thus



$$\begin{aligned}
 Z(y) &= \frac{y \sum_{r=0}^{2n} \frac{(y-a)^{r+n-1}}{(r+n-1)!} \frac{(2n)!}{(2n-r)!} a^{2n-r}}{3n \sum_{r=0}^{2n} \frac{(y-a)^{r+n}}{(r+n)!} \frac{(2n)!}{(2n-r)!} a^{2n-r}} \\
 Z(y) &= \frac{y \sum_{r=0}^{2n} \frac{(3n)!}{(r+n-1)!(2n-r)!} \frac{(y-a)^{r-1}}{a^r}}{3n \sum_{r=0}^{2n} \frac{(3n)!}{(r+n)!(2n-r)!} \frac{(y-a)^r}{a^r}} \\
 Z(y) &= \frac{y \sum_{r=0}^{2n} \frac{3n(3n-1)!}{(r+n-1)!(2n-r)!} \frac{(y-a)^{r-1}}{a^r}}{3n \sum_{r=0}^{2n} \frac{(3n)!}{(r+n)!(2n-r)!} \frac{(y-a)^r}{a^r}} \\
 Z(y) &= \frac{y \sum_{r=0}^{2n} \binom{3n-1}{2n-r} \left(\frac{y-a}{a}\right)^{r-1}}{a \sum_{r=0}^{2n} \binom{3n}{2n-r} \left(\frac{y-a}{a}\right)^r} = Z(y, n) \tag{19}
 \end{aligned}$$

The table 1 below illustrates the results of equation (19). Here $Z_{CS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}$ is due to (Carnahan and Sterling, [11]). η is the parking fraction (scale density)

Table 1
 $Z(y, N)$ for HSP with Selected Values of N from 2 to 50

η	y	$Z(y, N)$					Z_{CS}
		$N = 2$	$N = 5$	$N = 10$	$N = 20$	$N = 50$	target
0.019	$3a$	0.848	0.882	0.91	0.934	0.957	1.0815
0.065	$2a$	1.000	1.000	1.000	1.000	1.000	1.3103
0.1	$1.7365a$	1.108	1.077	1.045	1.018	1.002	1.521262
0.2	$1.3782a$	1.506	1.42	1.356	1.307	1.264	2.40625
0.3	$1.204a$	2.233	2.126	2.064	2.023	1.992	3.973761
0.4	$1.0939a$	4.128	4.015	3.959	3.924	3.900	6.925926
0.5	$1.0155a$	22.065	21.953	21.902	21.872	21.852	13

4.3 Other Potentials

4.3.1 The Inverse Twelfth Potential (ITP)

$$\phi(r) = \left\{ \varepsilon \left(\frac{\sigma}{r}\right)^{12} \quad r > 0 \right.$$

For this potential, $f'(0)$ has expressions that are divisible by zero. To avoid this situation, we modify the potential as

$$\phi(r) = \left\{ \varepsilon \left(\frac{\sigma}{r}\right)^{12} \quad r > \sigma \right.$$

The choice $\varepsilon = 4$ is a good fit for our model, thus $f(y) = y^{2n} \exp\left(-4\left\{\frac{a}{y}\right\}^{12}\right)$

4.3.2 The Lennard Jones Potential (LJP)

$$\phi(r) = \left\{ 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12} \right] \quad r > 0 \right.$$



Here also $f'(0)$ has expressions that are divisible by zero, thus we modify it to fit into our model

That is
$$\phi(r) = \left\{ 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right] \right. \quad r > \sigma$$

The value $\varepsilon = \frac{1}{2}$ is a good fit for our formula. Here $f(y) = y^{2n} \exp \left(-2 \left[\left(\frac{a}{y} \right)^6 - \left(\frac{a}{y} \right)^{12} \right] \right)$

The equation (12) gives us the result in table 2 for the case $N = 2$

Table 2

$Z(y, N)$ with $N = 2$ for various Potentials

3D	$N = 2$	This work			Target result
		$Z(y, N)$ for various Potentials			$Z(\eta)$
η	y	HSP	LJP	ITP	Z_{cs}
0.019	$3a$	0.848	0.998	1.214	1.0815
0.065	$2a$	1.000	1.332	1.593	1.3103
0.1	$1.7365a$	1.108	1.57	1.852	1.521262
0.2	$1.3782a$	1.506	2.428	2.717	2.40625
0.3	$1.204a$	2.233	3.933	4.021	3.973761
0.4	$1.0939a$	4.128	7.754	6.6	6.925926
0.5	$1.0155a$	22.065	41.225	24.843	13

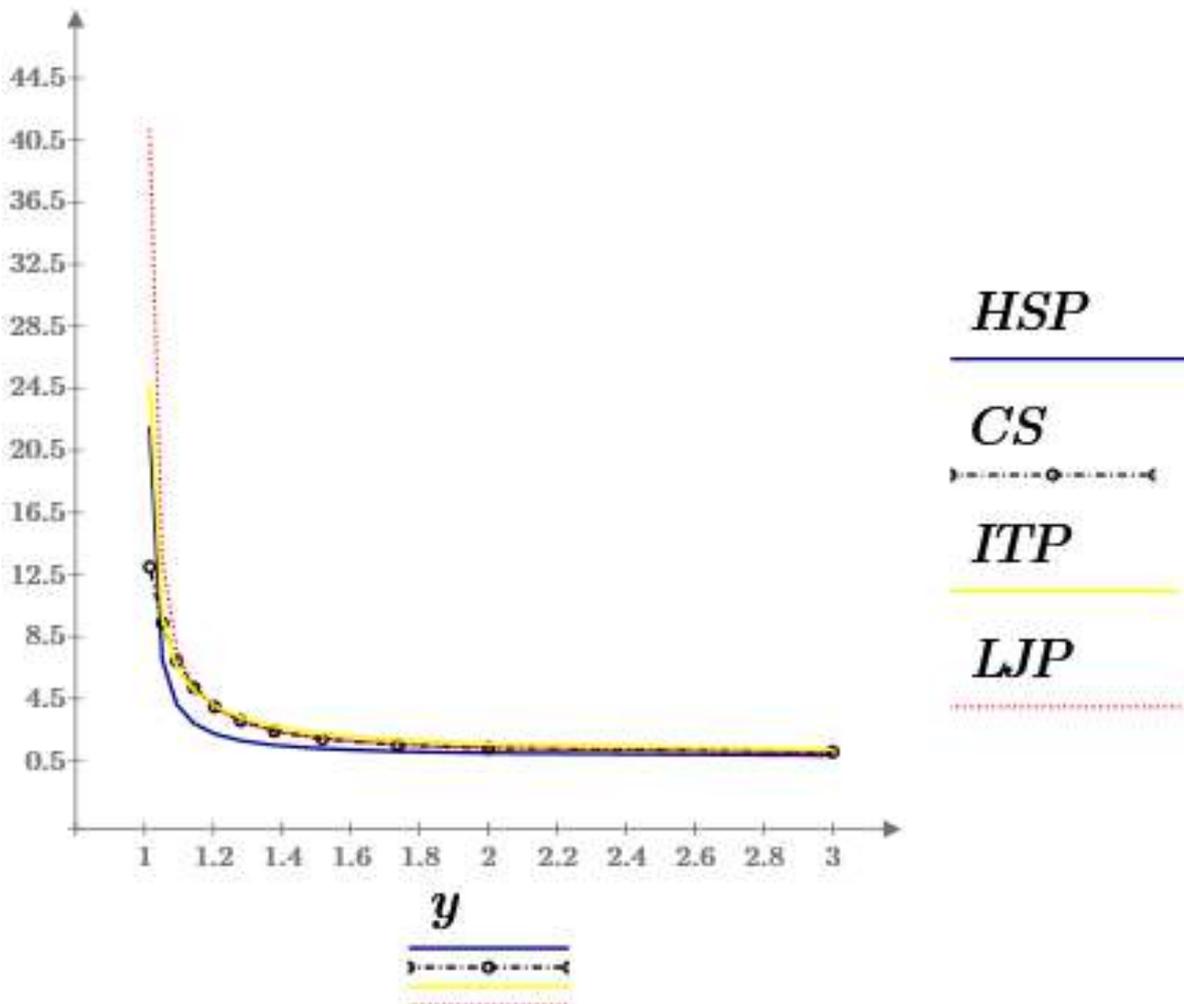


Figure 1

Line graph of $Z(y, N)$ against y for various EOS

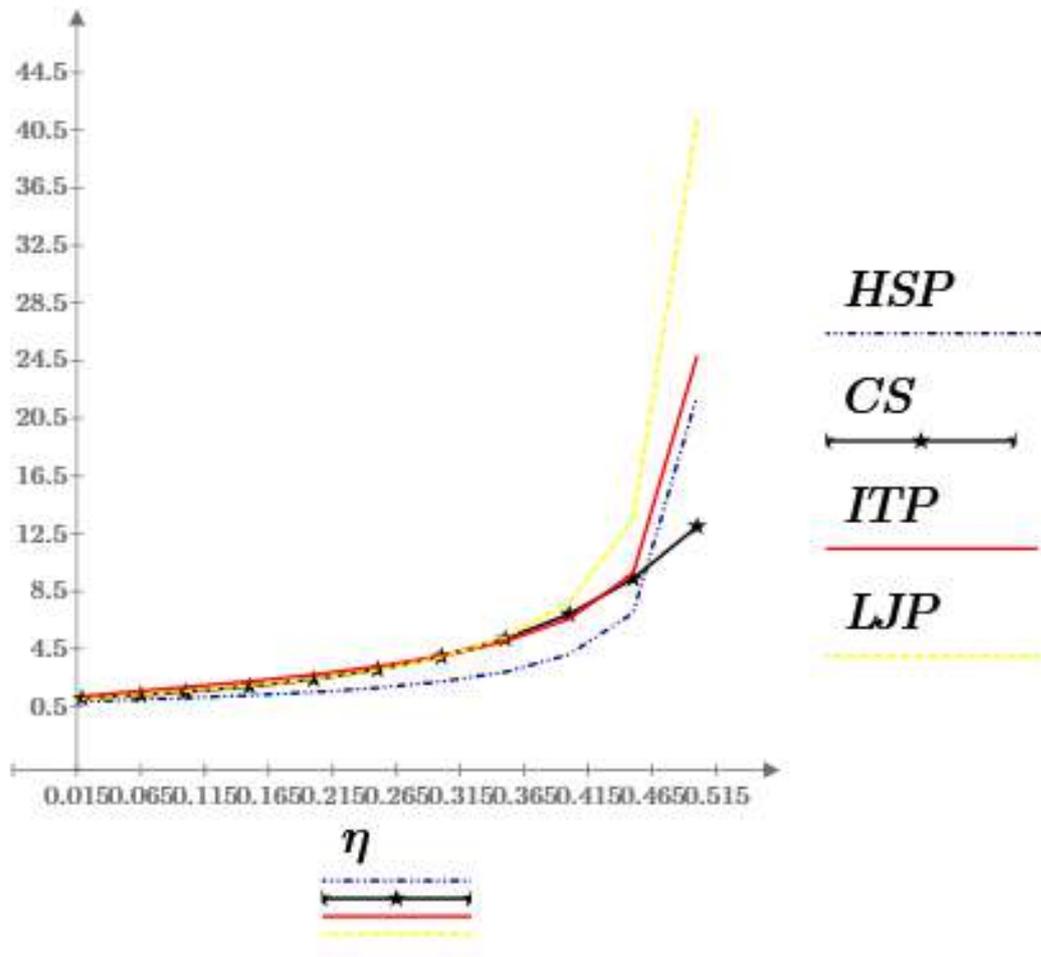
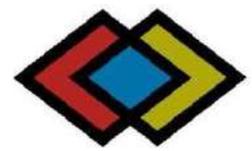


Figure 2

Line graph of $Z(\eta)$ against η for various EOS

4.4 Discussions

4.4.1 We have Comparatively better Results for Low Values of N

We noticed that from table 1, lower values of N give desirable results when compared to Z_{CS} . The case $N = 2$ is a simple case, which can be handled quite easily, to the extent that, it can be handled in a classroom.

4.4.2 Which Potential is more Realistic

From table 2, the product moment correlation between the Carnahan Sterling and the Hard Sphere Potential (HSP) gives $corr = 0.9406$, the Lennard – Jones potential (LJP) gives $corr = 0.9451$, whilst the Inverse twelfth potential (ITP) gives $corr = 0.9631$. This shows that there is a strong positive correlation for the three aforementioned potentials compared to Z_{CS} for the 3D case.

5. CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

The results here were derived from the configurational Integral which makes it important. With regards to the compressibility factor (Equation of state), the focus here is the case $= 2$, since by observation, it better agrees with Z_{CS} . Alternatively for high values of N , when $N \rightarrow \infty$, by computation $Z \rightarrow 1$.

5.2 Recommendations

The missing pieces in the study of fluids are the Partition Function and the Configurational Integral; we recommend that researchers interested in the study of fluids from Statistical Mechanics, Molecular Physics, or even Thermodynamics read this work.



REFERENCES

- [1] Turay, A. I. (2019). Partition functions for non-pairwise additive fluids, obtained via thermodynamic considerations (The three dimensional case). *African Journal of Pedagogy, Global Education Network Conference Proceedings*, 8, 1–15. <http://www.globaledunet.org>
- [2] Berberan-Santos, M. N., Bodunov, E. N., & Pogliani, L. (2008). The van der Waals equation: Analytical and approximate solutions. *Journal of Mathematical Chemistry*, 43(4), 1437–1457. <https://doi.org/10.1007/s10910-007-9272-4>
- [3] Kamerlingh, H. (2003). The virial equation of state. *Indian Journal of Chemical Technology*, 10, 564–572.
- [4] McQuarrie, D. A. (1976). *Statistical Mechanics*. Harper's Chemistry Series.
- [5] McDonald, I. R., & Hansen, J. P. (2006). *Theory of Simple Liquids*. Associated Press.
- [6] Reed, T. M., & Gubbins, K. E. (1973). *Applied Statistical Mechanics*. McGraw Hill.
- [7] Pathria, R. K., & Beale, P. D. (2011). *Statistical Mechanics*. Elsevier.
- [8] Reiss, H., Frisch, H. L., & Lebowitz, J. L. (1959). Statistical mechanics of rigid spheres. *Journal of Chemical Physics*, 31, 369.
- [9] Ree, F. H., & Hoover, W. G. (1964). Fifth and sixth virial coefficients for hard spheres and hard disks. *Journal of Chemical Physics*, 40, 939–950.
- [10] Hoover, W. G., & Ree, F. H. (1968). Melting transition and communal entropy for hard spheres. *Journal of Chemical Physics*, 49, 3609.
- [11] Carnahan, N. F., & Sterling, K. E. (1969). Equation of state for non-attracting rigid spheres. *Journal of Chemical Physics*, 51, 635–636.
- [12] Ferreira, M. A. M. (Ed.). (2021). *Theory and practice of mathematics and computer science* (Vol. 7, 1st ed.). Book Publisher International. <https://doi.org/> (if available) ISBN: 978-93-90768-00-4 (print), 978-93-90768-06-6 (online).
- [13] Wrede, R., & Spiegel, M. R. (2010). *Schaum's Outline of Advanced Calculus*. McGraw Hill.