

Estimation of pVT Virial Coefficients from Acoustic Measurements

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Abstract

The aim of this project is to find an alternative route for determining the second virial coefficient, B , and its densities, ρ , from acoustic measurements. pVT measurements is the most common method for determining B and ρ , however this method is subject to large errors at low temperatures, T , due to absorption, which affects the amount of substance, n , and hence the accuracy of pVT measurements. Acoustic measurements on the other hand do not have an absorption problem and can be related to pVT virial coefficients through a differential equation. This project will also explore the alternative routes of measurements and the methods for solving the differential equation.

KEY WORDS: Acoustic virial coefficients, densities, Lagrange interpolation method, Taylor series, Intermolecular forces

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1 Introduction

Unmarketable aromatics, storage facilities deterioration, pipeline corrosion and degradation of energy content are some of the problems caused by the change of natural gases into liquids due in part to errors in flow measurements⁴. Another reason why accurate measurements are important for the gas industries is that they buy in mass and sell to the consumers in volume. These are some of the reasons why the survival of the gas industries depends on accurately measuring the properties of gases.

1.1 Literature Review

One of the most important properties of gases is virial coefficients and they can be evaluated by various methods. This project will focus on evaluating the second virial coefficient of gases from acoustic measurements, from which the densities could be calculated.

First, it is imperative to have an understanding of what virial coefficients are and its relationship with statistical mechanics and intermolecular forces. We will also discuss some of the methods used for determining the virial coefficients. All of the concepts detailed above are very important and will be the foundation of this project.

At low densities (low pressures), intermolecular forces are negligible since on average gas molecules spend most of their time apart from each other. This behaviour is known as the ideal gas and is expressed mathematically by equation (1). As the pressure increases however, the molecules gather closer on average and our basic assumption breaks down. The virial coefficients account for the departure from ideality. It was added to the ideal equation as shown in equation (2) due to its sound theoretical base. B and C are the second and third virial coefficients and represent molecules interacting in pairs and triplets respectively. $\rho = n/V$ is the density.

$$pV_m/RT = 1 \tag{1}$$

$$pV_m/RT = 1 + B\rho + C\rho^2 + \dots \tag{2}$$

The second virial coefficient, $B(T)$, is related to intermolecular forces through the intermolecular potential energy, $U(r)$, as shown in equation (3).

$$B(T) = -2\pi \int_0^\infty (e^{-U(r)} - 1)r^2 dr \tag{3}$$

1.1.1 Statistical Mechanics

Statistical mechanics determines bulk, macroscopic properties from the knowledge of the force with which each molecule exerts on each other. This is why the study of intermolecular forces is important in statistical mechanics. The relationship between $U(r)$ and $B(T)$ can be derived using statistical mechanics. Statistical mechanics also plays an important role in relating virial coefficients and other thermodynamic properties². These properties include vapour pressure, boiling point, viscosity, heat of vaporisation, densities, enthalpies, rectilinear line and critical constant³. J.C Slater¹¹ starts his discussion on statistical mechanics by first commenting on thermodynamics. He states that thermodynamics is a simple, general, logical science that is based on two postulates; the first and second laws of thermodynamics. He went on to explain that the advantage statistical mechanics has over thermodynamics is that specific heat capacity or equation of state (for example) can be derived *directly* using statistical methods, whilst thermodynamics gives a connection between properties. He also stated that the second law is only a postulate, verified because it gave the correct result, whilst statistical mechanics uses simpler mechanical principles to arrive at the specific heat capacity or equation of state.

Derivation of the Second Acoustics Virial Coefficient using Statistical Mechanics

Neglecting orientation effects and writing the total potential energy interaction between two molecules i and j , at a distance r_{ij} apart, as $U(r_{ij})$, the whole potential energy of the gas is

$$\sum_{\text{pairs } ij} U(r_{ij})$$

The subscript under the summation is the reason why the potential energy and intermolecular pair potential are sometimes interchangeable. From statistical mechanics, the partition function has the expression

$$Q = \frac{1}{h^n} \int \cdots \int e^{-E/kT} dq_1 \cdots dp_n$$

Where h^n are cells of same volume, n is the number of coordinate and the momenta, E is the energy, dq_1 is the volume element and dp_n is the

volume element of phase *space*. To account for the identity of the molecule, the partition function must be multiplied by $(e/N)^N$

$$Q = \left(\frac{e}{Nh^3} \right)^N \int \cdot \int e^{-E/kT} dq_1 \cdot dp_{3N}$$

Q still contains a part that depends on momenta and another that depends on coordinates. The part depending on momenta is the same for a perfect gas, hence Q now has the expression

$$Q = \left[\frac{e(2\pi mkT)^{3/2}}{Nh^3} \right]^N \int \cdot \int e^{-\frac{\sum U(r_{ij})}{kT}} dq_1 \dots \quad (4)$$

The integral over the coordinate reduces to V^N in the case of a perfect gas. $dq_1 \dots$ can be written as $dx_1 dy_1 dz_1 \dots dx_N dy_N dz_N$. After integrating in steps and taking the factor that does not depend on the coordinates of the N th molecule outside the integration over its coordinates, the equation becomes

$$\int \int \int e^{-\frac{\sum U(r_{iN})}{kT}} dx_N dy_N dz_N$$

which can be rewritten as

$$\int \int \int dx_N dy_N dz_N - \int \int \int \left(1 - e^{-\frac{\sum U(r_{iN})}{kT}} \right) dx_N dy_N dz_N = V - W$$

if point $x_N y_N z_N$ is *far* from these molecules, $U(r_{iN})$ is small and the integrand is practically $1 - e^0 = 0$. Thus each contribution to this integrand from the immediate neighbourhood is

$$w = \int \int \int \left(1 - e^{-\frac{U(r_{iN})}{kT}} \right) dx dy dz$$

which can be rewritten as,

$$w = \int 4\pi r^2 \left(1 - e^{-\frac{U(r)}{kT}} \right) dr \quad (5)$$

hence $W = (N - 1)w$

Integral over coordinates in equation (4) gives;

$$[V - (N - 1)w][V - (N - 2)w] \cdots V$$

Taking the logarithm gives;

$$N \ln V + \sum_{s=0}^{N-1} \ln \left(1 - \frac{sw}{V} \right) \quad (6)$$

Replacing the summation with an integral gives;

$$N \ln V + \int_0^N \ln \left(1 - \frac{sw}{V} \right) ds = N \ln V - \frac{V}{w} \left(1 - \frac{Nw}{V} \right) \ln \left(1 - \frac{Nw}{V} \right) - N$$

The assumption that all our molecules are *well separated* is accurate only if Nw/V is small. Expanding the logarithm at the limit as

$$\ln \left(1 - \frac{Nw}{V} \right) = -\frac{Nw}{V} - \frac{1}{2} \left(\frac{Nw}{V} \right)^2 \cdots$$

Then substituting into equation (6) gives the following leading term

$$N \ln V - \frac{1}{2} N^2 \frac{w}{V} \cdots \quad (7)$$

Substituting equation (7) into (6) and then into the Helmholtz energy gives

$$A = -kT \ln Q = -\frac{3}{2} NkT \ln T - NkT \ln V + \frac{N^2 kT w}{2V} - NkT \left[\ln \left(\frac{2\pi m}{h^3} \right)^{3/2} k^{5/2} + 1 - \ln(Nk) \right]$$

Differentiating A with respect to V , gives the equation of state

$$p = - \left(\frac{\partial A}{\partial V} \right)_T = \frac{NkT}{V} + \frac{N^2 kT w}{2V^2}$$

Then substituting $Nk = nR$ and $N = nN_0$ gives

$$\frac{pV}{nRT} = 1 + \left(\frac{N_0 w}{2} \right) \left(\frac{n}{V} \right) = 1 + B(T) \left(\frac{n}{V} \right)$$

which shows that the second virial equation of state as $B(T) = \left(\frac{N_0 w}{2} \right)$. Substituting equation (5) into $B(T)$ gives the familiar expression

$$B(T) = \left(\frac{N_0 w}{2} \right) = 2\pi N_0 \int_0^\infty r^2 \left(1 - e^{-\frac{U(r)}{kT}} \right) dr = -2\pi N_0 \int_0^\infty \left(e^{-\frac{U(r)}{kT}} - 1 \right) r^2 dr$$

The second virial coefficient or equation of state $B(T)$ is exact despite all the approximations made, thus if further terms are retained they only affect third and higher virial coefficients.

1.1.2 Intermolecular forces

Since the end of the nineteenth century, a considerable amount of work has been devoted to the connection between the properties of bulk matter and intermolecular forces that have since become the ultimate aim of molecular theory of matter. Knowledge of the intermolecular forces is sufficient for the evaluation of all properties of bulk material. The representation of these forces between two molecules by means of potential energy function is one of the most important concepts. Consider two atoms, a and b , each composed of a positively charged nucleus that is surrounded by a negatively charged cloud interacting with one another. At infinite separation, the two atoms do not interact and the total energy, E_{tot} , is the sum of the energies of the individual atoms.

$$E_{tot}(\infty) = E_a + E_b$$

If the atom depends only on the separation of the two atoms and not their relative orientation, then the total energy at finite distance, r , is

$$E_{tot}(r) = E_a + E_b + U(r)$$

$U(r)$ the intermolecular pair potential energy function is

$$U(r) = E_{tot}(r) - E_a - E_b = E_{tot}(r) - E_{tot}(\infty)$$

i.e. the departure of the total energy from its value when the atoms are infinitely separated. Numerically, the energy difference is the work done in bringing two infinitely separated atoms to separation r and is expressed as

$$U(r) = \int_r^\infty F(r)dr, \text{ so that } F(r) = -\frac{dU}{dr}$$

where $F(r)$ is the force acting between the two atoms at separation r . By convention when $F(r)$ is positive/negative, the energy is repulsive/attractive.

1.1.3 Van der Waals equation of state

Van der Waals' work suggested the general form of intermolecular forces. Betts and Turner¹⁶ were able to show that an approximate second virial coefficient, $B(T)$, revealed the Physics it contained. This approximation reveals the van der Waals equation of state.

If the “hard-core” diameter is defined as the value of r for which $U(r) = kT$, so that d is a function of temperature but not a strong function to ensure that the energy of interaction rises sharply with decreasing separation. Then equation (3) can be solved as follows

$$B(T) = -2\pi \int_0^\infty (e^{-U(r)} - 1)r^2 dr \approx 2\pi \int_0^d r^2 dr + \frac{2\pi}{kT} \int_d^\infty U(r)r^2 dr = b - \frac{a}{kT}$$

where $a = 2\pi \int_d^\infty U(r)r^2 dr$ and $b = \frac{2\pi}{3}$. Using the above approximation and the Helmholtz free energy of system, we obtain an expression of

$$A = -kT \ln Q = -\frac{3}{2}NkT \ln \left(\frac{2\pi mkT}{h^2} \right) - NkT \ln \left(\frac{eV}{N} \right) - N^2 \frac{kT}{V} \left(\frac{a}{kT} - b \right)$$

Applying the approximate operation on A , gives $C_V = \frac{3}{2}Nk$ for non-interacting gas but

$$p = \frac{NkT}{V} - \frac{N^2 kT}{V^2} \left(\frac{a}{kT} - b \right)$$

and rearranging gives

$$p + \left(\frac{N}{V} \right)^2 a = \frac{NkT}{V} \left(1 + \frac{N}{V} b \right)$$

substituting $\left[1 + \left(\frac{N}{V} \right) b \right] \approx \left[1 - \left(\frac{N}{V} \right) b \right]^{-1}$ gives the familiar van der Waals equation of state

$$\left[p + \left(\frac{N}{V} \right) a \right] \left[1 - \left(\frac{N}{V} \right) b \right] = \frac{NkT}{V}$$

which is often written as

$$\left(p + \frac{a}{V_m} \right) (V_m - b) = RT$$

The importance of this equation lies in the prediction of a gas-liquid transition and the critical point at which pure substance exists, neither of which occurs for a perfect gas¹⁵. The van der Waals equation was an improvement on Maxwell and Boltzmann’s description of the kinetic behaviour of gases because it incorporated both attractive and repulsive forces. Maxwell assumed that the forces molecules exerted on each other were entirely repulsive, whilst Boltzmann’s series of intermolecular force laws all contained attractive components. Van der Waals equation is a combination of both forces because

the very existence of condensed phases of matter stems from the attractive forces between molecules and the small compressibility of these condensed phases arises from repulsion at short range. These forces are known as inter-molecular forces.

Conventionally, work on intermolecular potential makes use of potential parameters for conveniently characterising the potential. These parameters include the separation at which the potential energy is zero, σ , separation at which the energy is minimum, r_m , and the minimum energy, $-\epsilon$, where ϵ is the well depth. Since these parameters determine the scale rather than shape, they are distinct from other variable parameters.

1.1.4 Determining the intermolecular potential energy

The difficulties encountered while theoretically evaluating the intermolecular potential energy function lead to the heuristic approach in their determination. This approach usually begins with an analytic form that represents a relationship between the pair potential energy and the intermolecular separation. Using this assumed form, macroscopic properties are calculated with the aid of appropriate molecular theory and compared with experimental data. An agreement between the calculated macroscopic properties and experimental data confirms the correctness of the assumed potential energy function.

A similar approach can be found in [2], where Fitts explained that only few macroscopic physical properties could be calculated from only statistical mechanics and knowledge of pair potentials. These physical properties were the *second virial coefficient* - widely used because it can be exploited to determine the potential parameters. Some examples are the *Joule-Thompson coefficient* - a method which is dependent on the second-virial-coefficient-method; *transport properties* - a method which involves obtaining pair potential information from temperature variation of gaseous transport coefficient by means of the Chapman-Enskog theory; *crystal properties* - calculates the total internal energy U_0 of a crystal at absolute zero temperature; and *isotopic separation factor* - a method that obtains information about the pair potential from distribution of two isotopic species between their liquid and vapour phases, where the isotopic separation factor α is the useful quantity.

Although these methods yield crude estimates of the intermolecular potential energy, it however provides a means of estimating physical properties of the

same material with no experimental information available. One reason for this observation is that the analytical forms used in the representation of intermolecular pair potential energy function contains parameters such as σ or r_m , which determines the scale of the potential energy rather than its shape (they are distinct from other variable parameters).

1.1.5 Analytical forms for the intermolecular potential energy

$U(r)$ has many analytical forms. Some examples are the hard-sphere, square-well, Lennard-Jones¹, Exp-6 potential, Exp-6-8 potential, Morse, Guggenheim-McGlashan, Kihara potentials² etc.

1. Hard-sphere does not have the attractive part of its potential and stimulates the steep repulsive part of a realistic potential. $B(T)$ of hard spheres are independent of T .

$$U(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \quad (8)$$

Inserting $U(r)$ into equation (3) gives the following

$$\begin{aligned} B(T) &= -2\pi \int_0^\sigma (e^{-\infty} - 1)r^2 dr - 2\pi \int_\sigma^\infty (e^0 - 1)r^2 dr \\ &= -2\pi \int_0^\sigma (-r^2) dr \\ &= +2\pi \left[\frac{r^3}{3} \right]_0^\sigma \\ B(T) &= \frac{2\pi\sigma^3}{3} = b_0 \end{aligned} \quad (9)$$

2. Square-well potential includes the attractive part. It fits well for ordinary temperature.

$$U(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases} \quad (10)$$

Inserting equation (10) into equation (3) gives the following

$$B(T) = -2\pi \int_0^\sigma (e^{-\infty} - 1)r^2 dr - 2\pi \int_\sigma^{\lambda\sigma} (e^{\epsilon/kT} - 1)r^2 dr - 2\pi \int_{\lambda\sigma}^\infty (e^0 - 1)r^2 dr$$

$$\begin{aligned}
&= -2\pi \int_0^\sigma (-r^2) dr - 2\pi \int_\sigma^{\lambda\sigma} (e^{\epsilon/kT}) r^2 dr - 2\pi \int_\sigma^{\lambda\sigma} (-1)r^2 dr \\
&= +2\pi \left[\frac{r^3}{3} \right]_0^\sigma - 2\pi (e^{\epsilon/kT}) \left[\frac{r^3}{3} \right]_\sigma^{\lambda\sigma} + 2\pi \left[\frac{r^3}{3} \right]_\sigma^{\lambda\sigma} \\
&= \frac{2\pi\sigma^3}{3} - 2\pi (e^{\epsilon/kT} - 1) (\{\lambda\sigma\}^3 - \sigma^3) / 3 \\
&B(T) = b_0 \{1 - (\lambda^3 - 1)(e^{-\beta\epsilon} - 1)\} \tag{11}
\end{aligned}$$

As $\lambda \rightarrow 1$ or $\epsilon \rightarrow 0$, $B(T)$ approaches hard sphere, b_0 .

3. The Lennard-Jones potential is a more realistic representation of intermolecular potential. It was first suggested by Mie¹⁴, but Lennard-Jones¹⁵ applied this potential to calculate the second virial coefficients with $m = 4$ and n having values 8, 10, $13\frac{1}{2}$, 20, or 24. The general form of the Lennard Jones potential has the following expression

$$\begin{aligned}
U(r) &= \frac{n\epsilon}{n-m} \left(\frac{n}{m} \right)^{m/(n-m)} \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^m \right] \\
&= \frac{n\epsilon}{n-m} \left[\frac{m}{n} \left(\frac{r_m}{r} \right)^n - \left(\frac{r_m}{r} \right)^m \right]
\end{aligned}$$

when n is 12, the Lennard-Jones potential has the following expressions

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

$$U(r) = \epsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right]$$

r_m and σ are related by $r_m = 2^{1/6}\sigma$. The potential expressed in equation (12) is by far the most widely used analytical form.

Accurate B and C contain thermodynamic (thermal, caloric and acoustic) properties. However, the selection of an approximate potential causes the analysed virial coefficient to be influenced by the chosen potential. *Central to this project is a different approach, which involves numerical analysis that avoids the selection of an approximate potential in determining the virial coefficient from acoustic data.*

There are three main methods of finding the virial coefficients. They are the pVT method, the Joule-Thompson method and the acoustic method

1.1.6 pVT Method

Precise pressure-volume-temperature (pVT) measurements and analysis, results in the second virial coefficient⁵. This method involves four quantities instead of three as the name pVT might suggest. The molar volume, $V_m = V/n$, conceals the importance of the amount of gas, n .

$$\frac{V}{n} = V_m = \frac{1}{\rho} = \frac{RT}{p}(1 + B\rho + C\rho^2 + \dots) \quad (13)$$

$$\frac{1}{\rho}\left(\frac{p}{\rho RT} - 1\right) = B + C\rho + \dots \quad (14)$$

As equations (13) and (14) shows, analysing pVT measurements depends on knowing the densities, $\rho = n/V = V_m$. There is a great difficulty in measuring volume, V , and an even greater problem arises when measuring the amount of gas, n , due to the uncertainty in n . The requirement that n should be constant adds to this difficulty. This requirement becomes almost impossible at low reduced temperatures, T/T_c , because of absorption problems.

Although absorption is extremely difficult to model, this method is still being used today because of the ease with which pVT measurements relates with the virial coefficients as shown in equations (2), (13) and (14).

Alternatively, detailed comparison of isochoric^{3,4,6} heat capacity measurements are used in establishing virial equation of state, which contains $(\partial^2 p / \partial T^2)_\rho$ and thus $d^2 B / dT^2$ and $d^2 C / dT^2$.

1.1.7 Joule-Thompson Method

The Joule-Thompson approach⁵ comes from expansion the experiment on a gas. It offers a calomeric approach for determining the virial coefficient.

The second virial coefficient and its temperature derivative combine into function ϕ^0 .

$$\phi^0 = B(T) - T \frac{dB(T)}{dT} \quad (15)$$

ϕ^0 is related to Joule-Thompson coefficient at low-pressure limit $\mu_{JT} = (\partial T / \partial p)_h$, where h is the molar enthalpy.

$$\delta_T = (\partial h / \partial p)_T \quad (16)$$

$$\phi^0 = \lim_{p \rightarrow 0} \delta_T \quad (17)$$

$$\phi^0 = -c_p^0 \lim_{p \rightarrow 0} \mu_{JT} \quad (18)$$

δ_T is the isothermal throttling coefficient and c_p^0 is the molar isobaric heat capacity in an ideal state.

Although the Joule-Thompson approach provides a direct route for determining the virial coefficient, it is an ineffective method because of the problems encountered with the well-characterised steam experiments. It is encountered this problem at temperatures below 400K and above 500K, where the uncertainty values for water are not within the calculated ϕ^0 and $B(T)$ values. This suggests that larger molecules such as butane might have a bigger uncertainty problem when their experimental data are being characterised.

1.1.8 Acoustic Method

The acoustic method involves measuring the speed of sound, u , and the relative permittivity, ε . Both properties depend on frequency measurements, f , which can be measured accurately ($\Delta f/f < 1.10^{-8}$). This approach uses an apparatus that measures the following thermodynamic properties simultaneously⁴.

1. Location of phase boundary (p, ρ, T, x)
2. Relative permittivity, ε
3. Speed of sound, $u(T, \rho_n)$
4. Heat capacity at constant pressure, $c_p^{pg}(T)$

This method is more accurate than the pVT method because at low temperature, dispersion vanishes and the absorption problem disappears.

Absorption does not affect the accuracy of acoustic measurements⁷ because as equation (19) shows, the speed of sound, u , is independent of the amount of substance, n .

$$u^2(T, \rho_n) = (RT\gamma^{pg}/M)\{1 + \beta_a\rho_n + \gamma_a\rho_n^2 + \dots\} \quad (19)$$

To determine u , β_a , $B(T)$, first the zero-frequency speeds of sound are evaluated from frequency, f_{0n} , measurements of radial modes, then u is determined using equation (20).

$$u = 2\pi a \left[\frac{f_{0n} - \Delta f_{th} - \Delta f_t - \Delta f_{el} - \Delta f_{rel}}{v_{0n}} \right] \quad (20)$$

where a is the radius, v_{0n} is the eigenvalue for radial modes and $\Delta f_{th}, \Delta f_t, \Delta f_{el}$ are the correction terms

$$\frac{\Delta f_{rel}}{f} \approx 2(\gamma - 1)\Delta(\pi f\tau)^2\{1 - \Delta(1 + 3\gamma)/4\} \quad (21)$$

The heat capacity, c_p , and β_a can then be calculated from regression analysis of equation (19). An iterative approach, which involves analysis of density estimates while assuming perfect gas behaviour can be used to estimate β_a . The second virial coefficient, $B(T)$, can be derived from the β_a value, which can then be used to improve the estimated density.

Acoustic measurements provides exceptionally accurate results⁸ over wide temperature and density ranges including low T , where pVT measurements encounters problem of gas absorption. This suggests that the acoustic method is the best approach for determining the second virial coefficient. Another merit of this method is that acoustic measurements can be used in obtaining other thermodynamic properties just like the pVT method. For example, integrating the partial derivative equation shows that the speed of sound, u , is related to caloric and volumetric properties⁹. These properties rely on volumetric measurements being available at initial isotherm, hence acoustic measurements by themselves do not contain direct information about the molecular interaction.

1.2 Justification and approach

The literature review showed the rich history that surrounds the second virial coefficient with the likes of Maxwell, Boltzmann and Lennard-Jones who have, one way or another, affected the field of intermolecular potential energy and hence virial coefficients forever. During the review, the relationship between statistical mechanics and thermodynamics was shown using $A = -kT \ln Q$. The intermolecular forces and its analytical form were also mentioned. The elegant equations encountered begged for further investigation, probing questioning. Curiosity to understand is the justification for most scientists and it is the case for this project.

By showing through derivation, the relationship between the second virial coefficient and the intermolecular potential energy, the importance of statistical mechanics in this project was revealed.

Moving towards our objectives, the various analytical forms of the intermolecular potential energy and its relationship with measurable quantities were discussed. After which, the common experimental procedures and how

parameters are fitted onto potential to obtain the second virial coefficient were discussed.

Since this project involves the use of acoustic data, this method will become the core focus - in addition to discussing the method, all the relevant mathematical tools used for finding the second virial coefficient and its derivatives will also be discussed. Measurements of the acoustic virial coefficient are extremely accurate, so the problem now involves determining the second virial coefficient. This is why this project is analytical in nature and uses numerical tools like regression analysis to determine the virial coefficients and hence densities of different gases. Using a systematic approach, the attempt will be to determine the second virial coefficient accurately.

This approach will begin by using the square-well potential to determine estimates of the second virial coefficients of argon. Then using regression analysis, the corrected parameters a , b and c will be determined for argon and xenon. With these parameters known, the second virial coefficients will then be evaluated. Comparison between this method and the methods that eliminate the use of analytical form of intermolecular potential energy will be made.

From trying various methods of determining the derivatives of the acoustic virial coefficient, we stumbled upon a unique approach that uses Lagrange's interpolation method.

Lagrange interpolation method was discussed widely in literatures but research thus far has not shown any direct correlation between the methods used in literature and the approach this project takes.

2 Theory

2.1 Square-well Potential

The square-well potential is the starting point for this project. The potential expressed in equation (11) is simplified to include just three parameters - a , b and c .

$$B(T) = a + be^{c/T} \quad (22)$$

c/T replaces $\beta\varepsilon$ in equation (22) because the β parameter is dependent on temperature, T .

Equation (22) can be used to generate data required to test and develop the numerical analysis. Differentiating equation (22) with respect to temperature gives

$$B^{(1)}(T) = -\frac{bc}{T^2}e^{c/T} \quad (23)$$

$$B^{(2)}(T) = \frac{bc}{T^3}\left(2 + \frac{c}{T}\right)e^{c/T} \quad (24)$$

where the notation $B^{(n)} = d^n B/dT^n$ represents the derivative of B with respect to T , noting that $B^{(0)} = B$.

Numerical methods¹⁷ used in conjunction with β evaluates a , b and c parameters.

Since for an ideal gas $\gamma^{pg} = 5/3$, β can be calculated by using the following equations

$$\beta_a = 2B + 2(\gamma^{pg} - 1)TB^{(1)} + \{\gamma^{pg} - 1\}^2/\gamma^{pg}\}T^2B^{(2)} \quad (25)$$

$$\beta_a = 2B + (4/3)TB^{(1)} + (4/15)T^2B^{(2)} \quad (26)$$

2.2 Numerical Methods

2.2.1 Regression Analysis

Using regression analysis, the following can be determined:

$$\sigma^2(y) = \frac{1}{N-m} \sum (y_i - \hat{y}_i)^2 = \frac{\chi^2}{N-m} \quad (27)$$

where y_i is the experimental value and \hat{y}_i is the calculated value of y .

Adapting equation (27) to solve for $\sigma(\beta)$ gives

$$\sigma^2(\beta) = \frac{1}{N-m} \sum (\beta_i - \hat{\beta}_i)^2 = \frac{\chi^2}{N-m} \quad (28)$$

$$\sigma(\beta) = \sqrt{\frac{1}{N-m} \sum (\beta_i - \hat{\beta}_i)^2} = \sqrt{\frac{\chi^2}{N-m}} \quad (29)$$

2.2.2 Normal Equation

The normal equation arises from the merit function, χ^2 .

$$\chi^2 = \sum \left(\frac{y_i - \hat{y}_i}{\sigma_i} \right)^2 \quad (30)$$

Differentiating equation (30) with respect to the coefficient, a_j , leads to $m+1$ normal equations

$$\frac{\partial \chi^2}{\partial a_j} = 0; \quad j = 0, \dots, m \quad (31)$$

The normal equation provides a route for finding a , b and c parameters by reducing the coefficient's errors.

A generalised arbitrary function with many independent variables expressed as

$$\hat{y} = a_0 X_0 + a_1 X_1 + \dots + a_m X_m \quad (32)$$

has a general data set of form:

$$(X_{0i} X_{1i} X_{2i} \dots X_{mi}, y_i; \quad i = 1, \dots, N) \quad (33)$$

The normal equation can also be expressed as

$$\sum \left\{ \frac{\hat{y} X_j}{\sigma^2} \right\}_i = \sum \left\{ \frac{\hat{y}_i X_j}{\sigma^2} \right\}_i; \quad j = 1, \dots, m \quad (34)$$

and substituting equation (32) into equation (34) gives

$$a_0 \sum \left\{ \frac{X_0 X_j}{\sigma^2} \right\}_i + a_1 \sum \left\{ \frac{X_1 X_j}{\sigma^2} \right\}_i + \dots + a_m \sum \left\{ \frac{X_m X_j}{\sigma^2} \right\}_i = \sum \left\{ \frac{y_i X_j}{\sigma^2} \right\}_i; \quad j = 1, \dots, m \quad (35)$$

The matrix form of the normal equation is often written as

$$\tilde{C} \tilde{a} = \tilde{y} \quad (36)$$

When linear algebra is used to solve the equation, the inverse of the matrix generate the errors of the coefficients as part of the solution.

$$\tilde{C}^{-1} = \tilde{D} = \begin{pmatrix} \frac{\sigma^2(a_0)}{\sigma^2(y)} & \dots & \dots & \dots \\ \vdots & \frac{\sigma^2(a_1)}{\sigma^2(y)} & \dots & \dots \\ \vdots & \vdots & \ddots & \vdots \\ \dots & \dots & \dots & \frac{\sigma^2(a_m)}{\sigma^2(y)} \end{pmatrix} \quad (37)$$

The diagonal of the inverse gives the variance of the coefficients, while the off-diagonal gives the covariance of pairs of coefficients. Using the coefficient's errors, the coefficients a , b and c can be evaluated.

Next, the second virial coefficient has to be evaluated numerically and it involves using the Taylor series and the Lagrange interpolation method. This is an important step because as mentioned earlier it could eliminate the need for approximate potential.

2.3 Taylor Series

Taylor series evaluate virial coefficients at different temperatures from previous estimates of virial coefficients and its derivatives. Increasing the number of derivatives increases the accuracy of the estimated virial coefficient.

$$B(T + \delta T) = B(T_0) + B^{(1)}\delta T + (1/2)B^{(2)}(\delta T)^2 + \dots + (1/n!)B^{(n)}(\delta T)^n \quad (38)$$

$$B^{(1)}(T + \delta T) = B^{(1)}(T_0) + B^{(2)}\delta T + (1/2)B^{(3)}(\delta T)^2 + \dots \quad (39)$$

$$B^{(2)}(T + \delta T) = B^{(2)}(T_0) + \dots \quad (40)$$

Derivatives of β with respect to T , produces derivatives of virial coefficient.

$$d\beta/dT = (10/3)B^{(1)} + (28/15)TB^{(2)} + (4/15)T^2B^{(3)} \quad (41)$$

$$d^2\beta/dT^2 = (26/5)B^{(2)} + (12/5)TB^{(3)} + (4/15)T^2B^{(4)} \quad (42)$$

\vdots

$$d^6\beta/dT^6 = (90/5)B^{(6)} + (68/15)TB^{(7)} + (4/15)T^2B^{(8)} \quad (43)$$

$B^{(3)}, B^{(4)}, \dots, B^{(8)}$ can be evaluated by rearranging equations (41), (42), \dots , (43). If $B^{(1)}$ and $B^{(2)}$ are known in equation (41), then $d\beta/dT$ must be solved to determine $B^{(3)}$. One way of solving the derivative is by applying the Lagrange's interpolation method to experimental data β .

2.4 Lagrange's Interpolation Method

The finite difference method obtained by using the Taylor series is an effective method for solving the differential equation numerically. However this method seems to be limited to equally spaced grid points.

For three terms, the finite method for Taylor series gives the following:

$$y'_0 = (-3y_0 + 4y_1 - y_2)/2h \quad (44)$$

$$y'_0 = (-y_0 + y_2)/2h \quad (45)$$

$$y''_0 = (y_0 - 2y_1 + y_2)/h^2 \quad (46)$$

$$y''_1 = (y_0 - 2y_1 + y_2)/h^2 \quad (47)$$

Most experimental data are not usually equally spaced and hence the Taylor series finite method is not the most appropriate method of finding derivatives of β . Singh and Bhadauria¹⁰ used the Lagrange's interpolation formulae to obtain the finite difference formulae for unequally spaced sub-intervals.

2.4.1 Lagrange's Finite Difference Formulae

Function $f(x)$ of the Lagrange's interpolation formulae can be expressed as

$$f(x) = \sum_{j=0}^n l_j(x) f_j \quad (48)$$

For a three point finite difference formulae, Singh and Bhadauria set

$$x - x_0 = (s+1)h_1; x - x_1 = sh_1 \text{ and } x_1 - x_2 = sh_1 - h_2 \quad (49)$$

where intervals $[x_0, x_n]$ has n unequal sub-intervals width h_1, h_2, \dots, h_n such that

$$x_n = x_0 + \sum_{i=1}^n h_i$$

Substituting equation (49) into equation (48) gives

$$f(x) = \frac{s(sh_1 - h_2)}{h_1 + h_2} f(x_0) - \frac{(s+1)(sh_1 - h_2)}{h_2} f(x_1) + \frac{s(s+1)h_1^2}{h_2(h_1 + h_2)} f(x_2) \quad (50)$$

Differentiating equation (50) with respect to x gives

$$f'(x) = \frac{(2sh_1 - h_2)}{h_1(h_1 + h_2)} f(x)_0 - \frac{(2s+1)h_1 - h_2}{h_1 h_2} f(x)_1 + \frac{(2s+1)h_1}{h_2(h_1 + h_2)} f(x)_2 \quad (51)$$

Substituting $s = -1, 0$, and h_2/h_1 gives the formulae for the first order derivatives for $f(x)$ at points x_0, x_1 , and x_2

$$f'(x_0) = -\frac{(2h_1 + h_2)}{h_1(h_1 + h_2)} f(x)_0 + \frac{h_1 - h_2}{h_1 h_2} f(x)_1 - \frac{h_1}{(h_1 + h_2)h_2} f(x)_2 \quad (52)$$

$$f'(x_1) = -\frac{h_2}{h_1(h_1 + h_2)} f(x)_0 - \frac{h_1 - h_2}{h_1 h_2} f(x)_1 + \frac{h_1}{h_2(h_1 + h_2)} f(x)_2 \quad (53)$$

$$f'(x_2) = \frac{h_2}{h_1(h_1 + h_2)} f(x)_0 - \frac{h_1 - h_2}{h_1 h_2} f(x)_1 + \frac{h_1 + 2h_2}{h_2(h_1 + h_2)} f(x)_2 \quad (54)$$

The corresponding errors for equations (52), (53) and (54) are $\frac{h_1(h_1+h_2)}{6} f'''(\xi)$, $-\frac{h_1 h_2}{6} f'''(\xi)$ and $\frac{(h_1+h_2)h_2}{6} f'''(\xi)$ respectively. $f'''(\xi)$ is the third derivatives of $f(\xi)$ and ξ lies between the interval $[x_0, x_1]$.

3 Data

T/K	$\beta/cm^3 mol^{-1}$
90.0683	-228.97
99.5888	-182.023
118.8918	-120.889
149.8924	-67.088
189.9503	-30.345
240.2866	-5.132
273.1004	5.316
300.6045	11.966

(a) Argon

T/K	$\beta/cm^3 mol^{-1}$
190.163	-303.46
205.147	-254.7
225.014	-205.14
250.024	-159.15
273.164	-127.1
315.018	-85
360.002	-53.66

(b) Xenon

Table 1: Experimental results of Argon¹² and Xenon

4 Analytical Method

FORTRAN was the programming language. This language helped with the understanding of the theories discussed in chapter 2. Silverfrost FTN95 compiled the programs. PLATO editor modified the programs, edited the in-data and built the programs, which ran on MS-DOS. Microsoft Excel produced the graphs using the out-data.

4.1 Testing the Square-well Potential

First, we tested the square-well potential by writing a program as shown in chapter 9.1.1 from the appendix that calculates the second virial coefficient. Line 22 of the program corresponds to equation (22).

$$B(T) = a + be^{c/T}$$

```
22      B = a0 + a1*exp(a2/T(i))
```

where a , b and c parameters are labelled a_0 , a_1 and a_2 .

Using estimates of a_0 , a_1 , a_2 and Ewing & Trusler's temperature from table 1a as our in-data, we ran the program and it gave the following out-data.

```
Calc of B from Square Well
Coefficients are:  A =      155.0  B =      -120.0  C =      105.0
  T/K      B/cm^3 mol^-1
  90.07    -230.01
  99.59    -189.41
 118.89    -135.22
 149.89     -86.77
 189.95    -53.57
 240.29    -30.76
 273.10    -21.26
 300.60    -15.17
```

The second virial coefficients computed from these parameters were compared and contrasted with Ewing and Trusler's experimental results.

4.2 Fitting β to the Square-well Potential via Regression

Using theories from chapter 2, we wrote a program that fits β to the square-well potential as shown in Chapter 9.1.2.

Rearranging equation (27) gives the expression

$$\chi^2 = \sum (y - \hat{y}_i)^2 = \sum (\beta - \hat{\beta}_i)^2 \quad (55)$$

where β is the in-data from table 1. Equation (55) corresponds to lines 84 and 85, while line 89 corresponds to equation (29).

```
84      delta_y = B(i)-2.*B0 - (4./3.)*T(i)*B1 - ((4./15.)*T(i)**2)*B2
85      ch2 = ch2 + delta_y*delta_y
89      sigma_y = sqrt(ch2/float(N-m))
```

β is denoted by $B(i)$, while $B0$, $B1$ and $B2$ represents the zero, first and second derivatives of the second virial coefficient, calculated using the square-well potentials.

$B0$, $B1$ and $B2$ correspond to equations (22), (23) and (24) respectively. Equation (26) calculates $\hat{\beta}_i$. Lines 37 to 40 show these calculations.

```
37      B0 = a0 + a1*exp(a2/T(i))
38      B1 = -(a1*a2/T(i)**2)*exp(a2/T(i))
39      B2 = (a1*a2/T(i)**3)*(2. + a2/T(i))*exp(a2/T(i))
40      delta_y = 2.*B0 + (4./3.)*T(i)*B1 + ((4./15.)*T(i)**2)*B2
```

$delta_y$ denotes $\hat{\beta}_i$.

```
77      a0 = a0 -c(3,1)
78      a1 = a1 -c(3,2)
79      a2 = a2 -c(3,3)
```

Lines 77, 78 and 79 correct coefficients a_0 , a_1 and a_2 . $c(3,1)$, $c(3,2)$, $c(3,3)$ are the correction coefficients.

Subroutines DCMR(X,K,MAX,N,C,A,W,NCH) and ELIM(A,K,I) from lines 129 to 169 and lines 173 to 194 calculates the correction coefficients using equations (30) to (34).

The normal equations from lines 62 to 67 were evaluated using equation (31). Partial derivatives of χ^2 (equation (55)) with respect to the parameters (a_0 , a_1 and a_2) eliminates β since it is a constant - our in-data from table 1.

$$\frac{\partial \chi^2}{\partial a_0} = x(1, i) = -2$$

$$\frac{\partial \chi^2}{\partial a_1} = x(2, i) = \dots$$

$$\frac{\partial \chi^2}{\partial a_2} = x(3, i) = \dots$$

```

62      x(1,i) = -2.
63      x(2,i)=-2.*exp(a2/T(i))&
&+4.*a2*exp(a2/T(i))/(3.*T(i))-4.*a2*(2*T(i)+a2)*exp(a2/T(i))/(15.*T(i)**2)
64      x(3,i) = 4.*a1*(2.*T(i)-2.*a2)*exp(a2/T(i))/(6.*T(i)**2)&
65      &-4.*a1*(2.*T(i)+ a2)*exp(a2/T(i))/(15.*T(i)**2)&
66      &-4.*a1*a2*exp(a2/T(i))/(15.*T(i)**2)&
67      &-4.*a1*a2*(2.*T(i)+ a2)*exp(a2/T(i))/(15.*T(i)**3)

```

Hence, T and β from table 1 forms our in-data. Finally, the coefficients a_0 , a_1 and a_2 , which the program corrected were typed each time we ran the program.

Using the corrected coefficients, we calculated the second virial coefficient using the first program we wrote and compared it with Ewing and Trusler's results.

4.3 Taylor Series and Lagrange's Interpolation Method

In chapter 9.1.3 of the appendix, we compiled a program that avoids the use of any analytical form of $U(r)$ in determining the second virial coefficient. We did this by finding the derivatives of β using the Lagrange interpolation method. Then we rearranged equations (26) and (41) to (43) (*making the subject of the formula the highest derivative of the second virial coefficient*). These leading terms were added to the Taylor series to improve the second virial coefficient and its first derivative.

4.3.1 Lagrange Interpolation Method

Equations (52), (53) and (54) solve the derivatives of β with three or more data points. These equations correspond to x {first data}, x_1 {middle data} and x_2 {last data}.

For example, lines 30 to 40 correspond to equation (52). It finds the derivative of β at T_0 .

$$f'(x_0) = -\frac{(2h_1 + h_2)}{h_1(h_1 + h_2)}f(x)_0 + \frac{h_1 - h_2}{h_1 h_2}f(x)_1 - \frac{h_1}{(h_1 + h_2)h_2}f(x)_2$$

```

30      IF (i.EQ.1) THEN
31      f_0(i) = Beta(i)
32      f_1(i) = Beta(i+1)
33      f_2(i) = Beta(i+2)
34
35      h_1(i) = T(i+1)-T(i)
36      h_2(i) = T(i+2)-T(i+1)
37
38      dB_dT(i) = -(2*h_1(i)+h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
39      &+(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
40      &-(h_1(i))*f_2(i)/((h_1(i)+h_2(i))*h_2(i))

```

Lines 54 to 64 (equation (53)) evaluates the derivatives of β at the middle temperatures

$$f'(x_1) = -\frac{h_2}{h_1(h_1 + h_2)}f(x)_0 - \frac{h_1 - h_2}{h_1 h_2}f(x)_1 + \frac{h_1}{h_2(h_1 + h_2)}f(x)_2$$

```

54      ELSE
55      f_0(i) = Beta(i-1)
56      f_1(i) = Beta(i)
57      f_2(i) = Beta(i+1)
58
59      h_1(i) = T(i)-T(i-1)
60      h_2(i) = T(i+1)-T(i)
61
62      dB_dT(i) = -(h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
63      &-(h_1(i)-h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
64      &+(h_1(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))

```

While lines 42 to 52 (equation (54)) evaluates the derivative of β at the last temperature.

$$f'(x_2) = \frac{h_2}{h_1(h_1 + h_2)}f(x)_0 - \frac{h_1 - h_2}{h_1 h_2}f(x)_1 + \frac{h_1 + 2h_2}{h_2(h_1 + h_2)}f(x)_2$$

```

42      ELSE IF (i.EQ.Np+1) THEN
43      f_0(i) = Beta(i-2)
44      f_1(i) = Beta(i-1)
45      f_2(i) = Beta(i)
46
47      h_1(i) = T(i-1)-T(i-2)
48      h_2(i) = T(i)-T(i-1)
49
50      dB_dT(i) = (h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
51      &-(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
52      &+(h_1(i)+2*h_2(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))

```

Lagrange's interpolation method on previous derivatives of β gives higher derivatives of β . We calculated the errors for the first derivatives using the corresponding error formulae as shown on lines 268 to 292.

After numerically evaluating β , we rearranged equations (26) and (41) to (43) and made the highest derivatives of the second virial coefficient the leading term. Thus, equations (26) and (41) to (43) were expressed as

$$B^{(2)} = 15(\beta_a - 2B - (4/3)TB^{(1)})/4T^2 \quad (56)$$

which corresponds to line 297

```
297 B2(i)=(15.)*(Beta(i)-2.*B0(i)-(4./3.)*T(i)*B1(i))/(4*T(i)**2)
298 B3(i)=(15.)*(dB_dT(i)-(10./3.)*B1(i)-(28./15.)*T(i)*B2(i))/(4*T(i)**2)
299 B4(i)=(15.)*(dB_dTT(i)-(26./5.)*B2(i)-(12./5.)*T(i)*B3(i))/(4*T(i)**2)
303 B8(i)=(15.)*(dB_dTTTTT(i)-(90./5.)*B6(i)-(68./15.)*T(i)*B7(i))/(4*T(i)**2)
```

$$B^{(3)} = 15(d\beta/dT - (10/3)B^{(1)} - (28/15)TB^{(2)})/4T^2 \quad (57)$$

which corresponds to line 298

$$B^{(4)} = 15(d^2\beta/dT^2 - (26/5)B^{(2)} - (12/5)TB^{(3)})/4T^2 \quad (58)$$

which corresponds to line 299

$$B^{(8)} = 15(d^6\beta/dT^6 - (90/5)B^{(6)} - (68/15)TB^{(7)})/4T^2 \quad (59)$$

which corresponds to line 303

4.3.2 Taylor Series

Next, we determined the value of B and $B^{(1)}$ by expressing it as a Taylor series. By increasing the number of terms, expressed as the *second virial coefficients and its derivatives* (derived from the previous step), the values of B and $B^{(1)}$ improved. The Taylor series for B (equation (38)) and $B^{(1)}$ (equation (39)) corresponds to lines 304 to 305 and lines 306 to 307 respectively.

$$B(T + \delta T) = B(T_0) + B^{(1)}\delta T + (1/2)B^{(2)}(\delta T)^2 + \dots + (1/n!)B^{(n)}(\delta T)^n$$

$$B^{(1)}(T + \delta T) = B^{(1)}(T_0) + B^{(2)}\delta T + (1/2)B^{(3)}(\delta T)^2 + \dots$$

```
304 B0(i+1)=B0(i)+B1(i)*DT(i)+B2(i)*DT(i)**2/2+B3(i)*DT(i)**3/6+B4(i)*DT(i)**4/24&
305 &+B5(i)*DT(i)**5/120+B6(i)*DT(i)**6/720+B7(i)*DT(i)**7/5040+B8(i)*DT(i)**8/40320
306 B1(i+1)=B1(i)+B2(i)*DT(i)+B3(i)*DT(i)**2/2+B4(i)*DT(i)**3/6+B5(i)*DT(i)**4/24&
307 &+B6(i)*DT(i)**5/120+B7(i)*DT(i)**6/720+B8(i)*DT(i)**7/5040
```

Lines 304 to 307 provides an efficient way of increasing the terms of the Taylor series because FORTRAN codes allow sections of programs to be

made inactive - by simply putting an exclamation mark, *!*, in front. For example, if we want to include β , $d\beta/dT$ and $d^2\beta/dT^2$ and hence B^2 , B^3 and B^4 terms (*making terms B^5 to B^8 inactive*) in the Taylor expression, we put the exclamation mark in front of symbol & and $+B5(i)$ on lines 304 and 306 for B expression and $B^{(1)}$ respectively.

Finally, since we evaluated the difference between the square-well-second-virial-coefficient and the Lagrange-Taylor-series-second-virial-coefficient, our in-data must include a_0 , a_1 and a_2 . Equation (56) is the key equation with respect to the in-data, because it tells us most of the information the in-data should contain; they are B and $B^{(1)}$ at the start temperature, temperatures, T , and β . The Taylor series expression on lines 304 to 307 evaluates B and $B^{(1)}$ at all other temperatures.

The in-data for Xenon is

```
Calc of B using Square Well and Taylor
-87.205 0.51344 ... 246.573 -191.847 199.361 a0 a1 a2
360.002      -53.66
315.018      -85
273.164     -127.1
250.024     -159.15
225.014     -205.14
205.147     -254.7
190.163     -303.46
```

where -87.205 and 0.51344 are B and $B^{(1)}$ denoted by $B0(i)$ and $B1(i)$ in the program. The starting temperature is 360.002K. 246.573, -191.847 and 199.361 are the corrected coefficients. The two columns under -87.205 and 0.51344 are T and β data taken from table 1b.

5 Results

5.1 Table of Results

5.1.1 Testing the Square-well Potential

T/K	B/cm^3mol^{-1}
90.07	-230.01
99.59	-189.41
118.89	-135.22
149.89	-86.77
189.95	-53.57
240.29	-30.76
273.1	-21.26
300.6	-15.17

(a) Results for B using guess parameters $a_0 = 155$, $a_1 = -120$, $a_2 = 105$

T/K	B/cm^3mol^{-1}
90.0683	-221.162
99.5888	-183.581
118.8918	-132.689
149.8924	-86.165
189.9503	-53.554
240.2866	-30.781
273.1004	-21.223
300.6045	-15.087

(b) Ewing and Trusler¹²

Table 2: Results of B at various temperatures, T .

6 Discussion

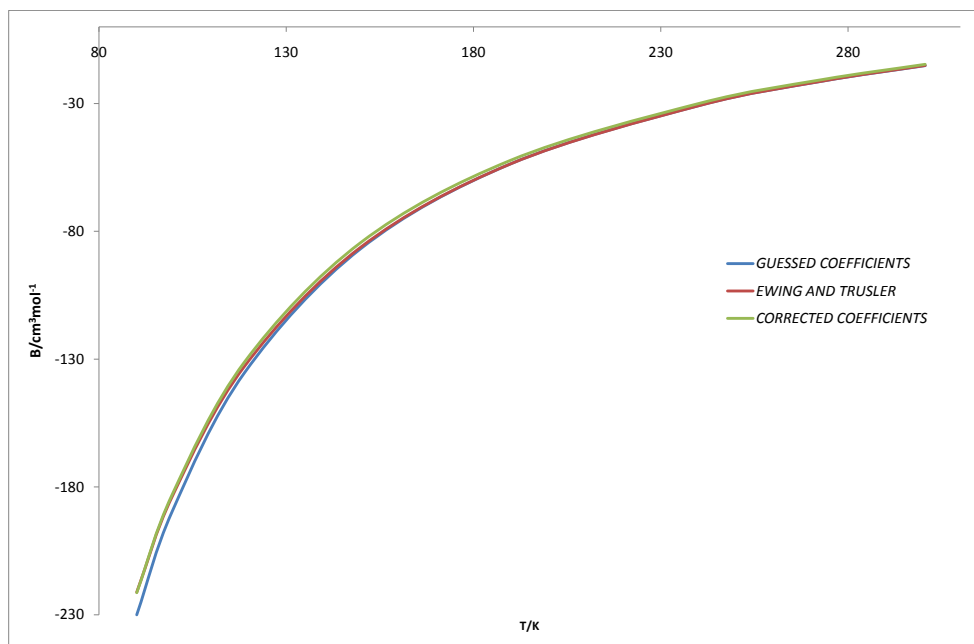


Figure 1: B against T .

The test that involved the square-well potential worked well as shown in Figure 1 when compared with Ewing and Trusler's. These similarities in values were unexpected and could be due to good guesses of the coefficients. When we fitted the square-well to β , the corrected coefficients we obtained were similar to our guessed coefficients as shown in Table 4 and there was a better fit when the corrected coefficients were used to determine B . *Why did this happen?*

The reason why the corrected coefficients from fitting the square-well potential works is because the potential provides a method for finding B , $B^{(1)}$, $B^{(2)}$ and hence β , which can be compared with the experimental β . From comparison, we can correct the coefficients by various methods. The method we used was regression analysis that involved the use of a normal equation to correct the coefficients. If we can find the exact coefficients, then the calculated β will fit our experimental β perfectly. Regression analysis on the square-well potential did not evaluate the exact coefficients but were

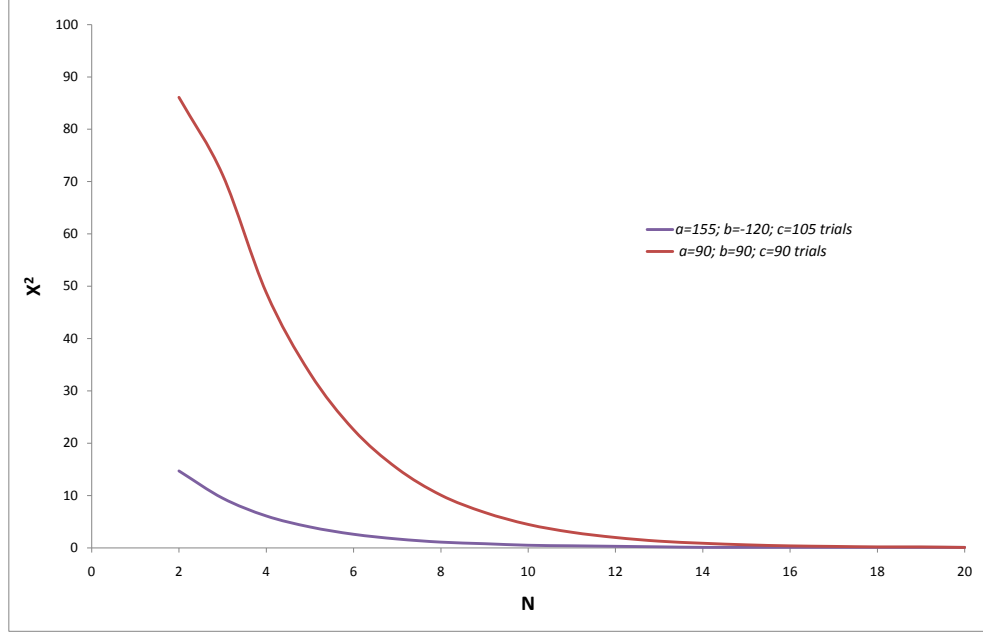


Figure 2: Illustration of χ^2 stability as the number of corrections, N , increases

close as shown in table 3, where $\sigma(\beta)$ at $N = 20$ is 0.12.

The program that fits β to the square-well potential failed when the trial coefficients $a = 50$, $b = 50$ and $c = 50$ were tested. The reason for this might lie in chapter 2.2.2 which discussed the normal equations.

Since χ^2 is a function of the coefficients, it forms a multidimensional surface. The least square equation represents the minimum of χ^2 . Near solutions, χ^2 surface has a positive curvature and its first partial derivative is zero. This is why we find the change in the coefficients, δa_i , that reduces χ^2 and as we move closer to the solution, χ^2 approaches its minimum. However if there are many local minimums, which may be the case when we chose $a = 50$, $b = 50$ and $c = 50$ coefficients, then the task of finding the global minimum becomes harder.

Nevertheless, figure 2 and 3 reinforces the observations we noted in our progress report - *The closer the trial parameters (a , b and c) were to the true parameters, the quicker the minimum of all three parameters were reached. The standard deviation and chi squared also stabilises ($\sigma(\beta) = 0.11$, $\chi^2 = 0.1$)*

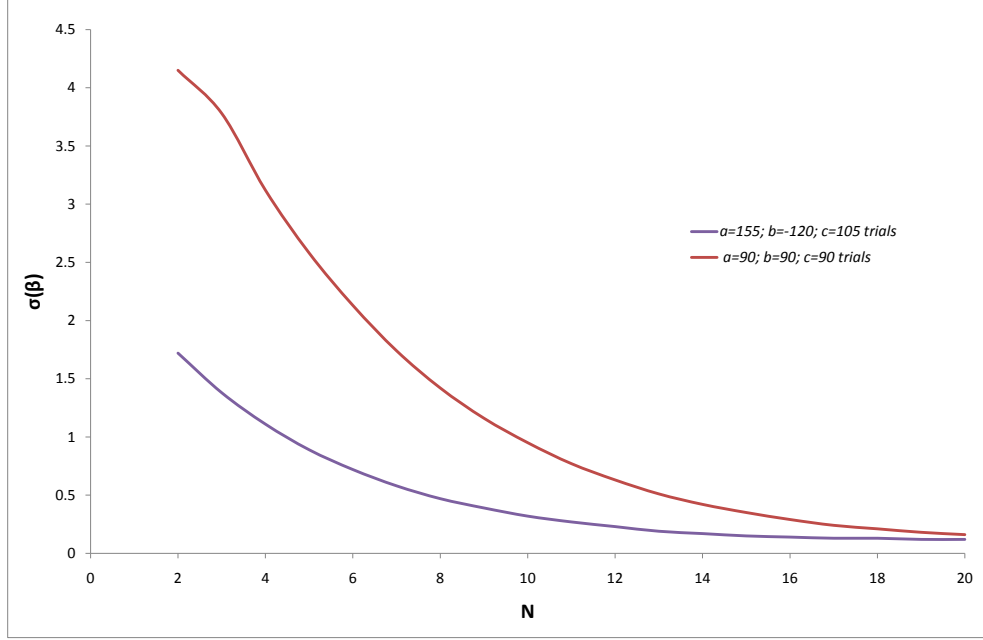


Figure 3: Illustration of $\sigma(\beta)$ stability as the number of corrections, N , increases

as *trial curve fits the true curve of β better*. The quick stabilisation of $\sigma(\beta)$ and χ^2 arises because fewer corrections are needed for the trial coefficients to move χ^2 to the global minimum. We also concluded in our progress report that δT intervals were by far the most important factor for calculating the most accurate second virial coefficients and its derivative. An explanation must be given as to why we have to revise that statement - explaining the reason we came to that conclusion and why we are now changing our mind.

The second half of our progress report dealt with Taylor series and hence required a means for calculating the derivatives of β to determine higher derivatives of B that are then inserted into the Taylor series. We did this by using the Taylor finite difference formulae, which we now know after further research (chapter 2.4 §1-3) is an inadequate method because our experimental data are not equally spaced. This meant that the derivatives we were calculating were inaccurate and hence the little improvements we noticed as we increased the number of terms in the Taylor series. With this discovery, we took a more cautious approach to ensure accuracy, which we did by comparing our numerically derived derivatives of β against the

derivatives derived from the square-well potential. Lagrange interpolation method proved to be an excellent method for deriving the derivatives of β .

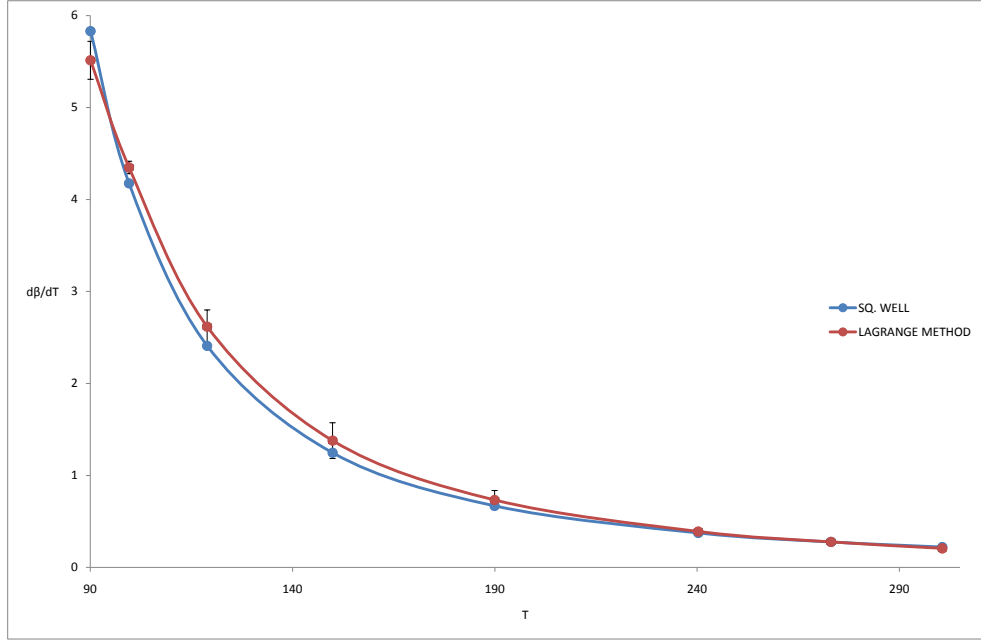


Figure 4: First derivative of β against T for Argon.

Figures 4 and 7 to 10 of the appendix shows a good agreement between the values of the derivatives of β obtained from the square-well potential (using the corrected coefficients) and the Lagrange interpolation method. The slopes of the first derivatives of β (figure 4) are almost exact. However as the order of derivative increases (figures 6 to 9 of the appendix), the Lagrange method's slope approaches zero. This observation is expected because at some point, the improvement to Taylor series has to stop (i.e. B or $B^{(1)}$ cannot be improved after certain number of terms has being added). The fifth derivative of β at first glance suggests a huge difference between the Lagrange and the square-well method, but on closer observation we noticed that the square-well potential fifth derivative is 7.5×10^{-5} at $T = 90\text{K}$, which is small. This means that the value $B^{(7)}$ will be small and the improvement made to B of the Taylor series will also be small, suggesting it is close to the point of convergence. For the Lagrange interpolation method, convergence is also close to the fifth derivative. We added the sixth derivative of β with

the aim of obtaining an accurate derivative.

There were improvements to B as we increased the Taylor series of B .

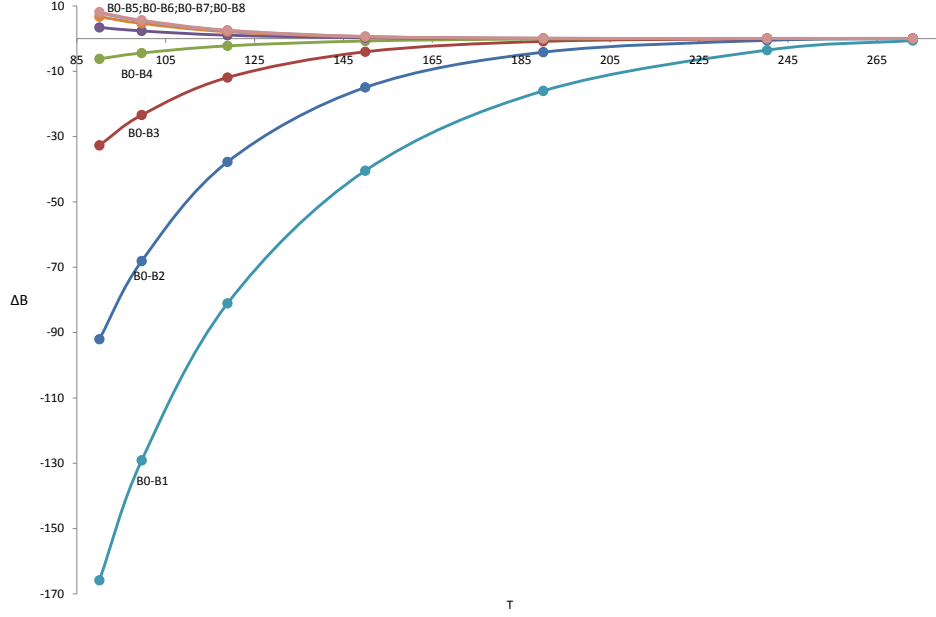


Figure 5: ΔB against Temperature for Argon. $\Delta B = B(\text{square} - \text{well potential}) - B(\text{Taylor})$.

Figure 5, clearly shows that B improved as we added more terms to the Taylor series of B . It began its convergence when third derivative of β or $B^{(5)}$ term was added to the Taylor expression.

The differences, ΔB , were big when the parameters a , b and c were roughly estimated as shown by figure 6. However at temperatures greater than 180K, ΔB approaches zero despite the fact that these three parameters ($a = 155$; $b = -120$; $c = 105$) were guessed. This small ΔB suggests similarities between the parameters we obtained and the parameters obtained by *Ewing and Trusler*. After fitting β to the square-well potential, ΔB got smaller on average, suggesting an improvement to the B value and hence the increased correlation noticed. This improved correlation could be attributed to the increased suitability of the correlated coefficients as opposed to those that had been

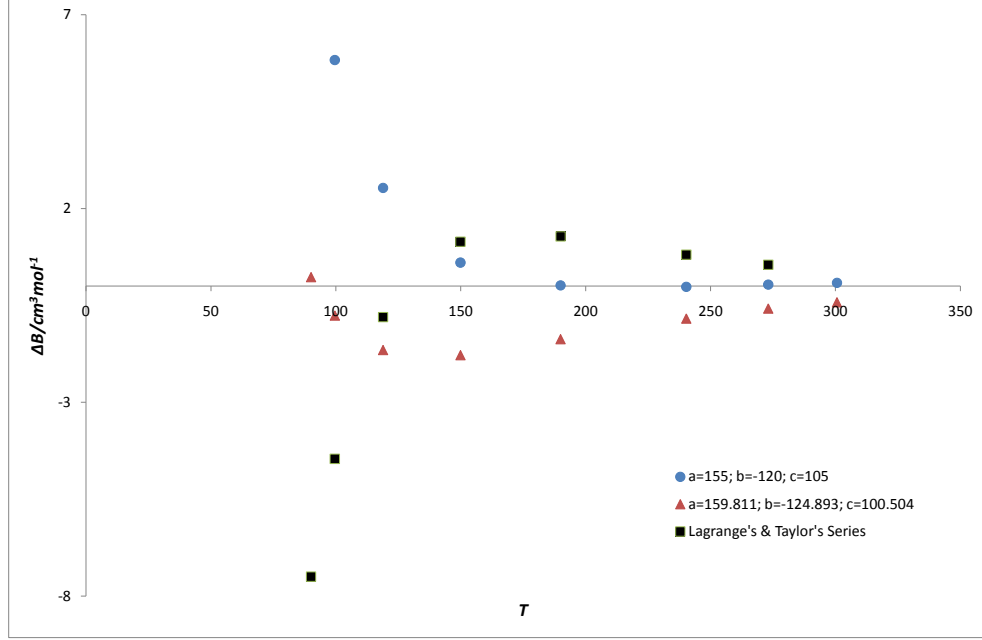


Figure 6: Differences ΔB between the second virial coefficient B for Argon. \bullet , square-well potential using estimates of a , b and c ; \blacktriangle , square-well potential using corrected a , b and c ; \blacksquare , Lagrange and Taylor's series. $\Delta B = B(\bullet, \blacktriangle, \blacksquare) - B(\text{Ewing \& Trusler})$

guessed. When Lagrange and Taylor's series were combined, the improvements were comparable to fitting β on the square-well potential and this justifies the inclusion of Lagrange-Taylor's method. The Lagrange-Taylor's method approach is perhaps the best estimator of B at temperatures between 300K and 120K. However, at lower temperatures, fitting β onto the square-well is the better approach because ΔB is smaller.

7 Conclusion

This project served in proving that the square-well potential and the Taylor series are two effective methods of finding the second virial coefficient of argon and xenon. Acoustic virial coefficients were our primary data as it could be measured accurately. The differences between these two methods

were less than $10\text{cm}^3\text{mol}^{-1}$ – 8.08 for argon and 0.15 for xenon. Although these results are good, the results can still be improved upon.

By using different sources of acoustic data for argon and xenon, it is possible to investigate the changes this has on a , b and c parameters, and perhaps reinforce the results obtained. Improvements can also be achieved by using more data and making comparison with the results collected. The project can be extended by investigating larger molecules and observing the effect it has on well-known parameters such as the well depth or a , b and c parameters. Further exploration could be done through the use of other analytical forms of potential, or by using quantum mechanics as a tool to find the second virial coefficient.

The problem encountered during the course of this project was that there were no absolute results in literatures. However, the absence of these absolute results succeeded in making the project fascinating. Acoustic measurements are perhaps one of the best way of attaining the highest accuracy when trying to achieve the ultimate goal of determining the second virial coefficient exactly. Reaching this goal will involve either finding the exact potential or the best mathematical tools for solving this problem or both.

8 References

1. McQuarrie, D. A., 2002. Statistical Mechanics. University Science Books.
2. Fitts, D. D. 1966. Statistical Mechanics: A Study of Intermolecular Forces. Annual Review of Physical Chemistry, 17, 59.
3. Mastroianni, M. J., Stahl, R. F. & Sheldon, P. N. 1978. Physical and Thermodynamic Properties Of 1,1,2-Trifluorotrichloroethane (R-113). Journal of Chemical and Engineering Data, 23, 113-118.
4. Goodwin, A. R. H. & Hill, J. A. 2009. Thermophysical Properties of Natural Gas Components: Apparatus and Speed Of Sound In Argon. Journal of Chemical and Engineering Data, 54, 2758-2771.
5. Harvey, A. H. & Lemmon, E. W. 2004. Correlation for the Second Virial Coefficient of Water. Journal of Physical and Chemical Reference Data, 33, 369-376.
6. Abdulagatov, A. I., Kaplun, A. B., Meshalkin, A. B., Abdulagatov, I. M. & Stepanov, G. V. 2002. Second Caloric Virial Coefficients for Real Gases and Combined Spherical Symmetric Potential for Simple Molecular Interactions. Journal of Chemical Thermodynamics, 34, 2049-2072.

7. Ewing, M. B. & Trusler, J. P. M. 1989. Speeds of sound in CF₄ Between 175-K and 300-K Measured with a Spherical Resonator. *Journal of Chemical Physics*, 90, 1106-1115.
8. Abdulagatov, A. I., Kaplun, A. B., Meshalkin, A. B., Abdulagatov, I. M. & Stepanov, G. V. 2002. Second Caloric Virial Coefficients for Real Gases and Combined Spherical Symmetric Potential For Simple Molecular Interactions. *Journal Of Chemical Thermodynamics*, 34, 2049-2072.
9. Monago, K. O. 2005. An equation of state for gaseous argon determined from the speed of sound. *Chemical Physics*, 316, 9-19.
10. Singh, A. K. & Bagadauria, B. S. 2009. Finite Difference Formulae for unequal Sub-Intervals Using Lagrange's Interpolation Formula. *International Journal of Mathematical Analysis*, Vol. 3, 17, 815-827
11. Slater, J. C. 1939. *Introduction to Chemical Physics*.
12. Ewing, M. B. & Trusler, J. P. M. 2000. Primary Acoustic Thermometry between T=90K and T=300K. *Journal of Chemical Thermodynamics*, 32, 1229-1255.
13. Lennard-Jones, J. E. 1924. On the Determination of Molecular Fields. II. From Equation of State of a Gas. *Proceedings of the Royal Society of London*. 106, 463-477
14. Mie, G. 1903.
15. Maitland, G. C., Rigby, M., Smith, E. B., Wakeham, W. A. 1981. *Intermolecular forces: Their origin and determination*. Oxford University Press
16. Betts D. S., Turner, E. T. 1992. *Introductory Statistical Mechanics*.
17. Ewing, M. B. 2009. *Numerical and Analytical Methods - Regression Analysis Lecture Notes*

9 Appendix

9.1 Programs

9.1.1 Using the Square-well Potential to Calculate the Virial Coefficient

```

1  program calc_b
2  implicit none
3  integer, parameter:: Nmax=50
4  integer:: i, iostat, endoffile
5  real:: a0,a1 ,a2
6  real:: B, T
7  character(len=30):: fin, fout
8  character (len=65):: title
9      call files(2, fin,fout,9,10)
10     read(9,'(A)') title
11     write(6,'(A)') title
12     write(10,'(A)') title
13     read(9,*) a0,a1,a2
14     write(6,'(3F10.1)') a0,a1,a2
15     write(10,'(A,3(A,F10.1))') 'Coefficients are: ', 'A =', a0,' B =',a1,' C =',a2
16     write(6,'(6X,A,5x,A)') 'T/K', 'B/cm^3 mol^-1'
17     write(10,'(6X,A,5x,A)') 'T/K', 'B/cm^3 mol^-1'
18     Do i = 1,Nmax
19         read(9,*,iostat = endoffile) T
20         If (endoffile /=0 .OR. T == 0.0 ) then
21             Exit
22         else
23             B = a0 + a1*exp(a2/T(i))
24             write(6,100) T,B
25             write(10,100) T,B
26         end if
27     End Do
28
29     !      write(2,'(F10.2,F10.0)') T,B
30     100 format(F10.2,F10.0)
31 end program calc_b
32
33 subroutine files(N_expect,fin, fout, nin, nout)
34
35 ! Set up file streams
36
37 implicit none
38
39     character(len=30):: fin, fout
40
41     integer::N_files, nin, nout, N_expect
42
43     integer, external::IARGC
44
45     external:: GETARG
46
47     N_files = IARGC()
48
49     if(N_files.EQ.N_expect) then
50
51         call GETARG(1,fin)
52

```

```

53      call GETARG(2,fout)
54
55      else
56
57          write(6,'(I3,A)') N_expect,' files are required'
58
59          WRITE(6,'('' Enter file name for input'')')
60
61          READ(5,'(A)') fin
62
63          WRITE(6,'('' Enter file name for output'')')
64
65          READ(5,'(A)') fout
66
67      end if
68
69      open (nin, FILE=fin, STATUS='OLD')
70
71      open (nout, FILE=fout)
72
73      write(6,'(A,2(/T10,A,I3,A,A)/)') ' The active streams are:', &
74
75      &                '5 = keyboard; ',nin, ' = ', fin,&
76
77      &                '6 = screen; ',nout, ' = ',fout
78
79  end subroutine files

```

9.1.2 Fitting β to the Square-well by Regression

```

1  PROGRAM calc_b
2  ! fits Beta to square well by non-linear regression
3  IMPLICIT NONE
4  INTEGER, PARAMETER:: Nmax=50, iter_max = 20, m=3, k=4
5  INTEGER:: i, iostat, endoffile, N, j, l
6  REAL:: a0,a1,a2, yin, xin, z
7  REAL:: DELTA_Y, ch2, ch2_old
8  REAL:: B(Nmax), T(Nmax), sigma_y, B0, B1, B2
9  REAL*8:: x(K,Nmax), A(K,K), C(K,K), W(Nmax)
10 CHARACTER (len=30):: fin, fout
11 CHARACTER (len=65):: title, coef, cols_head
12 CALL files(2, fin,fout,9,10)
13 READ(9,'(A)') title
14 WRITE(6,'(A)') title
15 WRITE(10,'(A)') title
16 READ(9,'(A)') coef
17 WRITE(6,'(A)') coef
18 WRITE(10,'(A)') coef
19 read(9,'(A)') cols_head
20
21 !      Read the data
22      DO i = 1,Nmax
23          READ(9,*,iostat = endoffile) xin, yin
24          IF (endoffile /=0 .OR. xin == 0.0 ) THEN
25              EXIT
26          ELSE
27              T(i) = xin
28              B(i) = yin
29          END IF
30      END DO
31

```

```

32      N = i -1
33      WRITE (6,'(A)') 'Enter starting values for a_0 a_1 and a_2'
34      READ(5,*) a0, a1, a2
35      ch2=0.0
36      DO i = 1, N
37          B0 = a0 + a1*exp(a2/T(i))
38          B1 = -(a1*a2/T(i)**2)*exp(a2/T(i))
39          B2 = (a1*a2/T(i)**3)*(2. + a2/T(i))*exp(a2/T(i))
40          delta_y = 2.*B0 + (4./3.)*T(i)*B1 + ((4./15.)*T(i)**2)*B2
41          delta_y = B(i) - delta_y
42          ch2 = ch2 + delta_y*delta_y
43      !      write(6,'(4F10.2,',' Beta: ',2F10.1)') T(i), B0, B1, B2, B(i), delta_y
44      END DO
45
46
47      sigma_y = sqrt(ch2/float(N-m))
48      j=0
49      ch2_old = ch2
50      ! print column headings
51      WRITE(6,'(T2,A,5x,A,11x,A,11x,A,13x,A,8x,A)') 'n', 'a0', 'a1', 'a2', 'Ch2', 's(B)'
52      WRITE(6,100) j, a0,a1,a2,ch2,sigma_y
53      100 format(I2,F10.3,3x,F10.3,3x,F10.3,3x,F10.1,3x,F10.2)
54      DO j=1, iter_max
55          IF (xin < 0.0) EXIT
56
57      !      set up normal equations
58
59      DO i = 1, N
60          delta_y = 2.*B0 + (4./3.)*T(i)*B1 + ((4./15.)*T(i)**2)*B2
61          delta_y = B(i) - delta_y
62          x(1,i) = -2.
63          x(2,i) = -2.*exp(a2/T(i))+4.*a2*exp(a2/T(i))/(3.*T(i))-4.*a2*(2*T(i)+a2)*exp(a2/T(i))
64          x(3,i) = 4.*a1*(2.*T(i)-2.*a2)*exp(a2/T(i))/(6.*T(i)**2)&
65          &-4.*a1*(2.*T(i)+ a2)*exp(a2/T(i))/(15.*T(i)**2)&
66          &-4.*a1*a2*exp(a2/T(i))/(15.*T(i)**2)&
67          &-4.*a1*a2*(2.*T(i)+ a2)*exp(a2/T(i))/(15.*T(i)**3)
68          B0 = a0 + a1*exp(a2/T(i))
69          B1 = -(a1*a2/T(i)**2)*exp(a2/T(i))
70          B2 = (a1*a2/T(i)**3)*(2. + a2/T(i))*exp(a2/T(i))
71          delta_y = 2.*B0 + (4./3.)*T(i)*B1 + ((4./15.)*T(i)**2)*B2
72          x(k,i) = B(i) - delta_y
73          w(i) = 1.
74      END DO
75      CALL DCMR(x,k,m,N,C,A,W,8)
76      ch2=0.0
77      a0 = a0 -c(3,1)
78      a1 = a1 -c(3,2)
79      a2 = a2 -c(3,3)
80      DO i = 1, N
81          B0 = a0 + a1*exp(a2/T(i))
82          B1 = -(a1*a2/T(i)**2)*exp(a2/T(i))
83          B2 = (a1*a2/T(i)**3)*(2. + a2/T(i))*exp(a2/T(i))
84          delta_y = B(i)-2.*B0 - (4./3.)*T(i)*B1 - ((4./15.)*T(i)**2)*B2
85      ch2 = ch2 + delta_y*delta_y
86      END DO
87
88
89      sigma_y = sqrt(ch2/float(N-m))
90      WRITE(6,100) j, a0,a1,a2,ch2,sigma_y
91      WRITE(10,100) j, a0,a1,a2,ch2,sigma_y
92      If (abs(c(3,1)/a0) < 1.0e-6 .and. abs(c(3,2)/a1) < 1.0e-6 .and. abs(c(3,3)/a2) < 1.0e-6)
93      If (abs(ch2_old-ch2) < 0.1) exit

```

```

94         end do
95
96
97     end program calc_b
98
99     subroutine files(N_expect,fin, fout, nin, nout)
100     ! Set up file streams
101     implicit none
102     character(len=30):: fin, fout
103     integer::N_files, nin, nout, N_expect
104     integer, external::IARGC
105     external:: GETARG
106     N_files = IARGC()
107     if(N_files.EQ.N_expect) then
108         call GETARG(1,fin)
109         call GETARG(2,fout)
110     else
111         write(6,'(I3,A)') N_expect,' files are required'
112         WRITE(6,'('' Enter file name for input'')')
113         READ(5,'(A)') fin
114         WRITE(6,'('' Enter file name for output'')')
115         READ(5,'(A)') fout
116     end if
117     open (nin, FILE=fin, STATUS='OLD')
118     open (nout, FILE=fout)
119     write(6,'(A,2(/T10,A,I3,A,A)/)') ' The active streams are:', &
120     & '5 = keyboard; ',nin,' = ', fin,&
121     & '6 = screen; ',nout,' = ',fout
122 end subroutine files
123
124 SUBROUTINE DCMR(X,K,MAX,N,C,A,W,NCH)
125 IMPLICIT none
126 real*8:: X(K,N),A(K,K),C(K,K),W(N)
127 real*8::T,SS,S,SW
128 integer::J,I,L,NCH,N,MAX,K
129     SW=0.D00
130     IF (MAX.EQ.0.OR.MAX.GE.K) MAX=K-1
131     IF (MAX.GE.N) MAX=N-1
132     DO L=1,N
133         SW=SW+1.D00/(W(L)*W(L))
134     end do
135     SW=DBLE(N)/SW
136     C(K,K)=SW
137     DO I=1,K
138         DO J=K,1,-1
139             A(I,J)=0.0D00
140             IF(J.GE.I) THEN
141                 DO L=1,N
142                     A(I,J)=A(I,J)+X(I,L)*X(J,L)*SW/(W(L)*W(L))
143                 end do
144             ELSE
145                 A(I,J)=A(J,I)
146             END IF
147         end do
148     end do
149     DO I=1,MAX
150         CALL ELIM(A, K, I)
151         S=A(K,K)/DBLE(N-I)
152         SS=DSQRT(DABS(S))
153         DO L=1,I
154             C(I,L)=A(L,K)
155             C(L,I+1)=DSQRT(DABS(S*A(L,L)))

```

```

156         end do
157         C(K,I)=A(K,K)
158         !WRITE(NCH,303) I,SS
159 303     FORMAT(//T1,I3,T6,'terms',T15,'Std Deviation of y = ',D16.8)
160         !WRITE(NCH,300)
161 300     FORMAT(T16,'Coef',T29,'Std Deviation',T48,'t',T63,'t2')
162         DO L=1,I
163             T=C(I,L)/C(L,I+1)
164             !WRITE(NCH,301) L,C(I,L),C(L,I+1),T,T*T
165         end do
166 301     FORMAT(T1,'x-',I2,T11,2D16.8,2D12.4)
167     end do
168     RETURN
169 END SUBROUTINE DCMR
170
171
172
173     SUBROUTINE ELIM(A, K, I)
174     ! Subroutine eliminates the row I from the matrix and replaces it with the
175     ! corresponding elements of the inverse
176     implicit none
177     real*8:: A(K,K), EL, P
178     integer:: J, L, I, K
179     P=1.0D00/A(I,I)
180     DO L=1,K
181         A(I,L)=A(I,L)*P
182     end do
183     A(I,I)=P
184     DO J=1,K
185         IF(J.NE.I) THEN
186             EL=A(J,I)
187             DO L=1,K
188                 IF(L.EQ.I) A(J,L)=0.0D00
189                 A(J,L)=A(J,L)-EL*A(I,L)
190             end do
191         END IF
192     end do
193     RETURN
194 END

```

9.1.3 Finding the Virial Coefficient via the Taylor Series and the Lagrange's Interpolation Method

```

1  !Calculates B(n){Squarewell}-B(n){Taylor}
2  implicit none
3  integer, parameter::Nmax=50, Np=6 !number of points minus 1
4  integer:: i, endoffile
5  real::xin,yin,D_1,D_0,a0,a1,a2
6  REAL, DIMENSION(Nmax):: T,B0,B1,B2,B3,B4,B5,B6,B7,B8,Beta,dB_dT,dB_dTT,dB_dTTT,sigma_dB_dT
7  REAL, DIMENSION(Nmax):: dB_dTTTT,dB_dTTTTT,dB_dTTTTTT,B,DT,f_0,f_1,f_2,h_1,h_2,f3_zeta
8  character(len=30):: fin, fout
9  character (len=65):: title
10     call files(2, fin,fout,9,10)
11     read(9,'(A)') title
12     write(6,'(A)') title
13     write(10,'(A)') title
14     read(9,*) B0(1),B1(1),B2(1),B3(1),a0,a1,a2
15     write(6,'(3F10.1)') B0(1),B1(1),B2(1),B3(1),a0,a1,a2
16     write(10,'(A,3(A,F10.1))') 'Virial coeff and derivatives: ', 'A =', B0(1), '
B =',B1(1), ' C =',B2(1)
17     write(6,'(T1,A,6x,A,8x,A,8x,A,8x,A,7x,A,10x,A,7x,A)') 'T/K', 'B2(i)', 'B3(i)', 'D0(i)', 'D1(i)

```



```

18   write(10,'(T1,A,6x,A,8x,A,8x,A,8x,A,7x,A,10x,A,7x,A)') 'T/K', 'B2(i)', 'B3(i)', 'D0(i)', 'D1(i)'
19   Do i = 1,Nmax
20       READ(9,*,iostat = endoffile) xin,yin
21       IF (endoffile /=0 .OR. xin == 0.0 ) THEN
22           EXIT
23       ELSE
24           T(i) = xin
25           Beta(i)=yin
26       END IF
27   END DO
28   !LANDRANDE'S INTERPOLATION METHOD
29   DO i=1, Np+1
30       IF (i.EQ.1) THEN
31           f_0(i) = Beta(i)
32           f_1(i) = Beta(i+1)
33           f_2(i) = Beta(i+2)
34
35           h_1(i) = T(i+1)-T(i)
36           h_2(i) = T(i+2)-T(i+1)
37
38           dB_dT(i) = -(2*h_1(i)+h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
39           &+(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
40           &-(h_1(i))*f_2(i)/((h_1(i)+h_2(i))*h_2(i))
41
42       ELSE IF (i.EQ.Np+1) THEN
43           f_0(i) = Beta(i-2)
44           f_1(i) = Beta(i-1)
45           f_2(i) = Beta(i)
46
47           h_1(i) = T(i-1)-T(i-2)
48           h_2(i) = T(i)-T(i-1)
49
50           dB_dT(i) = (h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
51           &-(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
52           &+(h_1(i)+2*h_2(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
53
54       ELSE
55           f_0(i) = Beta(i-1)
56           f_1(i) = Beta(i)
57           f_2(i) = Beta(i+1)
58
59           h_1(i) = T(i)-T(i-1)
60           h_2(i) = T(i+1)-T(i)
61
62           dB_dT(i) = -(h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
63           &-(h_1(i)-h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
64           &+(h_1(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
65       END IF
66   END DO
67   !For the second derivative we carry out the same method
68   DO i=1, Np+1
69       IF (i.EQ.1) THEN
70           f_0(i) = dB_dT(i)
71           f_1(i) = dB_dT(i+1)
72           f_2(i) = dB_dT(i+2)
73
74           h_1(i) = T(i+1)-T(i)
75           h_2(i) = T(i+2)-T(i+1)
76
77           dB_dTT(i) = -(2*h_1(i)+h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
78           &+(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
79           &-(h_1(i))*f_2(i)/((h_1(i)+h_2(i))*h_2(i))

```

```

80
81     ELSE IF (i.EQ.Np+1) THEN
82         f_0(i) = dB_dT(i-2)
83         f_1(i) = dB_dT(i-1)
84         f_2(i) = dB_dT(i)
85
86         h_1(i) = T(i-1)-T(i-2)
87         h_2(i) = T(i)-T(i-1)
88
89         dB_dTT(i) = (h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
90         &-(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
91         &+(h_1(i)+2*h_2(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
92
93     ELSE
94         f_0(i) = dB_dT(i-1)
95         f_1(i) = dB_dT(i)
96         f_2(i) = dB_dT(i+1)
97
98         h_1(i) = T(i)-T(i-1)
99         h_2(i) = T(i+1)-T(i)
100
101         dB_dTT(i) = -(h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
102         &-(h_1(i)-h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
103         &+(h_1(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
104     END IF
105 END DO
106
107 !For the THIRD derivative we carry out the same method
108
109 DO i=1, Np+1
110     IF (i.EQ.1) THEN
111         f_0(i) = dB_dTT(i)
112         f_1(i) = dB_dTT(i+1)
113         f_2(i) = dB_dTT(i+2)
114
115         h_1(i) = T(i+1)-T(i)
116         h_2(i) = T(i+2)-T(i+1)
117
118         dB_dTTT(i) = -(2*h_1(i)+h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
119         &+(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
120         &-(h_1(i))*f_2(i)/((h_1(i)+h_2(i))*h_2(i))
121
122     ELSE IF (i.EQ.Np+1) THEN
123         f_0(i) = dB_dTT(i-2)
124         f_1(i) = dB_dTT(i-1)
125         f_2(i) = dB_dTT(i)
126
127         h_1(i) = T(i-1)-T(i-2)
128         h_2(i) = T(i)-T(i-1)
129
130         dB_dTTT(i) = (h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
131         &-(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
132         &+(h_1(i)+2*h_2(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
133
134     ELSE
135         f_0(i) = dB_dTT(i-1)
136         f_1(i) = dB_dTT(i)
137         f_2(i) = dB_dTT(i+1)
138
139         h_1(i) = T(i)-T(i-1)
140         h_2(i) = T(i+1)-T(i)
141

```

```

142         dB_dTTT(i) = -(h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
143         &-(h_1(i)-h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
144         &+(h_1(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
145     END IF
146 END DO
147 !For the FOURTH derivative we carry out the same method
148 DO i=1, Np+1
149     IF (i.EQ.1) THEN
150         f_0(i) = dB_dTTT(i)
151         f_1(i) = dB_dTTT(i+1)
152         f_2(i) = dB_dTTT(i+2)
153
154         h_1(i) = T(i+1)-T(i)
155         h_2(i) = T(i+2)-T(i+1)
156
157         dB_dTTTT(i) = -(2*h_1(i)+h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
158         &+(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
159         &-(h_1(i))*f_2(i)/((h_1(i)+h_2(i))*h_2(i))
160
161     ELSE IF (i.EQ.Np+1) THEN
162         f_0(i) = dB_dTTT(i-2)
163         f_1(i) = dB_dTTT(i-1)
164         f_2(i) = dB_dTTT(i)
165
166         h_1(i) = T(i-1)-T(i-2)
167         h_2(i) = T(i)-T(i-1)
168
169         dB_dTTTT(i) = (h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
170         &-(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
171         &+(h_1(i)+2*h_2(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
172
173     ELSE
174         f_0(i) = dB_dTTT(i-1)
175         f_1(i) = dB_dTTT(i)
176         f_2(i) = dB_dTTT(i+1)
177
178         h_1(i) = T(i)-T(i-1)
179         h_2(i) = T(i+1)-T(i)
180
181         dB_dTTTT(i) = -(h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
182         &-(h_1(i)-h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
183         &+(h_1(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
184     END IF
185 END DO
186 !For the FIFTH derivative we carry out the same method
187 DO i=1, Np+1
188     IF (i.EQ.1) THEN
189         f_0(i) = dB_dTTTT(i)
190         f_1(i) = dB_dTTTT(i+1)
191         f_2(i) = dB_dTTTT(i+2)
192
193         h_1(i) = T(i+1)-T(i)
194         h_2(i) = T(i+2)-T(i+1)
195
196         dB_dTTTTT(i) = -(2*h_1(i)+h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
197         &+(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
198         &-(h_1(i))*f_2(i)/((h_1(i)+h_2(i))*h_2(i))
199
200     ELSE IF (i.EQ.Np+1) THEN
201         f_0(i) = dB_dTTTT(i-2)
202         f_1(i) = dB_dTTTT(i-1)
203         f_2(i) = dB_dTTTT(i)

```

```

204
205         h_1(i) = T(i-1)-T(i-2)
206         h_2(i) = T(i)-T(i-1)
207
208         dB_dTTTTT(i) = (h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
209         &-(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
210         &+(h_1(i)+2*h_2(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
211
212     ELSE
213         f_0(i) = dB_dTTTTT(i-1)
214         f_1(i) = dB_dTTTTT(i)
215         f_2(i) = dB_dTTTTT(i+1)
216
217         h_1(i) = T(i)-T(i-1)
218         h_2(i) = T(i+1)-T(i)
219
220         dB_dTTTTT(i) = -(h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
221         &-(h_1(i)-h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
222         &+(h_1(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
223     END IF
224 END DO
225 !For the SIXTH derivative we carry out the same method
226 DO i=1, Np+1
227     IF (i.EQ.1) THEN
228         f_0(i) = dB_dTTTTT(i)
229         f_1(i) = dB_dTTTTT(i+1)
230         f_2(i) = dB_dTTTTT(i+2)
231
232         h_1(i) = T(i+1)-T(i)
233         h_2(i) = T(i+2)-T(i+1)
234
235         dB_dTTTTTT(i) = -(2*h_1(i)+h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
236         &+(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
237         &-(h_1(i))*f_2(i)/((h_1(i)+h_2(i))*h_2(i))
238
239     ELSE IF (i.EQ.Np+1) THEN
240         f_0(i) = dB_dTTTTT(i-2)
241         f_1(i) = dB_dTTTTT(i-1)
242         f_2(i) = dB_dTTTTT(i)
243
244         h_1(i) = T(i-1)-T(i-2)
245         h_2(i) = T(i)-T(i-1)
246
247         dB_dTTTTTT(i) = (h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
248         &-(h_1(i)+h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
249         &+(h_1(i)+2*h_2(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
250
251     ELSE
252         f_0(i) = dB_dTTTTT(i-1)
253         f_1(i) = dB_dTTTTT(i)
254         f_2(i) = dB_dTTTTT(i+1)
255
256         h_1(i) = T(i)-T(i-1)
257         h_2(i) = T(i+1)-T(i)
258
259         dB_dTTTTTT(i) = -(h_2(i))*f_0(i)/(h_1(i)*(h_1(i)+h_2(i)))&
260         &-(h_1(i)-h_2(i))*f_1(i)/(h_1(i)*h_2(i))&
261         &+(h_1(i))*f_2(i)/(h_2(i)*(h_1(i)+h_2(i)))
262     END IF
263 END DO
264
265 !WE TO FIND THE ERROR SIGMA IN dB/dT

```

```

266
267
268      DO i=1, Np+1
269          IF (i.EQ.1) THEN
270              h_1(i) = T(i+1)-T(i)
271              h_2(i) = T(i+2)-T(i+1)
272
273              f3_zeta(i) = dB_dTTT(i+1)
274
275              sigma_dB_dT(i) = h_1(i)*(h_1(i)+h_2(i))*f3_zeta(i)/6.
276
277          ELSE IF (i.EQ.Np+1) THEN
278              h_1(i) = T(i-1)-T(i-2)
279              h_2(i) = T(i)-T(i-1)
280
281              f3_zeta(i) = dB_dTTT(i-1)
282
283              sigma_dB_dT(i) =(h_1(i)+h_2(i))*h_1(i)*f3_zeta(i)/6.
284
285          ELSE
286              h_1(i) = T(i)-T(i-1)
287              h_2(i) = T(i+1)-T(i)
288
289              f3_zeta(i) = dB_dTTT(i)
290
291              sigma_dB_dT(i) =-h_1(i)*h_2(i)*f3_zeta(i)/6.
292          END IF
293      END DO
294
295      DO i = 1,Np!+1
296          DT(i)=T(i+1)-T(i)
297          B2(i)=(15.)*(Beta(i)-2.*B0(i)-(4./3.)*T(i)*B1(i))/(4*T(i)**2)
298          B3(i)=(15.)*(dB_dT(i)-(10./3.)*B1(i)-(28./15.)*T(i)*B2(i))/(4*T(i)**2)
299          B4(i)=(15.)*(dB_dTT(i)-(26./5.)*B2(i)-(12./5.)*T(i)*B3(i))/(4*T(i)**2)
300          B5(i)=(15.)*(dB_dTTT(i)-(38./5.)*B3(i)-(44./15.)*T(i)*B4(i))/(4*T(i)**2)
301          B6(i)=(15.)*(dB_dTTTT(i)-(158./15.)*B4(i)-(52./15.)*T(i)*B5(i))/(4*T(i)**2)
302          B7(i)=(15.)*(dB_dTTTTT(i)-(70./5.)*B5(i)-(20./5.)*T(i)*B6(i))/(4*T(i)**2)
303          B8(i)=(15.)*(dB_dTTTTTT(i)-(90./5.)*B6(i)-(68./15.)*T(i)*B7(i))/(4*T(i)**2)
304          B0(i+1)=B0(i)+B1(i)*DT(i)+B2(i)*DT(i)**2/2+B3(i)*DT(i)**3/6+B4(i)*DT(i)**4/24+B5(i)*DT(i)
305          &+B7(i)*DT(i)**7/5040+B8(i)*DT(i)**8/40320
306          B1(i+1)=B1(i)+B2(i)*DT(i)+B3(i)*DT(i)**2/2+B4(i)*DT(i)**3/6+B5(i)*DT(i)**4/24+B6(i)*DT(i)
307          &+B8(i)*DT(i)**7/5040
308          B(i) = a0 + a1*exp(a2/T(i+1))
309          B(i+1) = -(a1*a2/T(i+1)**2)*exp(a2/T(i+1))
310          D_0=B(i)-B0(i+1)
311          D_1=B(i+1)-B1(i+1)
312          !write(6,100) T(i), dB_dT(i), dB_dTT(i), dB_dTTT(i), dB_dTTTT(i), dB_dTTTTT(i), dB_dTTTTTT(i)!,
313          !write(10,100) T(i), dB_dT(i), dB_dTT(i), dB_dTTT(i), dB_dTTTT(i), dB_dTTTTT(i), dB_dTTTTTT(i)!,
314          write(6,100) T(i+1), B0(i+1), B1(i+1), D_0, D_1
315          write(10,100) T(i+1), B0(i+1), B1(i+1), D_0, D_1
316      End Do
317
318      100 format(F7.3,G13.5,G13.5,G13.5,G13.5,G13.4,G13.4,G12.4)
319      end program Taylor_1
320
321      subroutine files(N_expect,fin, fout, nin, nout)
322
323      ! Set up file streams
324
325      implicit none
326
327      character(len=30):: fin, fout

```

```

328
329     integer::N_files, nin, nout, N_expect
330
331     integer, external::IARGC
332
333     external:: GETARG
334
335     N_files = IARGC()
336
337     if(N_files.EQ.N_expect) then
338
339         call GETARG(1,fin)
340
341         call GETARG(2,fout)
342
343     else
344
345         write(6,'(I3,A)') N_expect,' files are required'
346
347         WRITE(6,'('' Enter file name for input'')')
348
349         READ(5,'(A)') fin
350
351         WRITE(6,'('' Enter file name for output'')')
352
353         READ(5,'(A)') fout
354
355     end if
356
357     open (nin, FILE=fin, STATUS='OLD')
358
359     open (nout, FILE=fout)
360
361     write(6,'(A,2(/T10,A,I3,A,A)/)') ' The active streams are:', &
362
363     &                '5 = keyboard; ',nin,' = ', fin,&
364
365     &                '6 = screen; ',nout,' = ',fout
366
367 end subroutine files

```

9.2 Tables

9.2.1 Fitting β to the Square-well Potential

N	a_0	a_1	a_2	χ^2	$\sigma(\beta)$
1	153.661	-118.757	104.161	23.9	2.19
2	154.774	-119.865	103.459	14.7	1.72
3	155.719	-120.808	102.886	9.5	1.38
4	156.499	-121.585	102.421	6.1	1.11
5	157.138	-122.224	102.043	4	0.89
6	157.662	-122.746	101.737	2.6	0.72
7	158.089	-123.173	101.488	1.7	0.58
8	158.437	-123.52	101.287	1.1	0.47
9	158.72	-123.803	101.125	0.8	0.39
10	158.95	-124.033	100.993	0.5	0.32
11	159.137	-124.219	100.887	0.4	0.27
12	159.288	-124.37	100.801	0.3	0.23
13	159.41	-124.492	100.731	0.2	0.19
14	159.509	-124.591	100.675	0.1	0.17
15	159.589	-124.671	100.629	0.1	0.15
16	159.654	-124.736	100.593	0.1	0.14
17	159.706	-124.788	100.563	0.1	0.13
18	159.749	-124.831	100.539	0.1	0.13
19	159.783	-124.865	100.52	0.1	0.12
20	159.811	-124.893	100.504	0.1	0.12

Table 3: Results from fitting β on a square-well potential. N is the number of corrections, while a_0 , a_1 and a_2 are the coefficients.

	a_0	a_1	a_2
Corrected coefficients	159.811	-124.893	100.504
Guessed coefficients	155	-120	105
Difference	4.811	4.893	-4.496

Table 4: Results of the corrected and guessed coefficients.

T/K	$B/cm^3 mol^{-1}$
90.07	-221.39
99.59	-182.82
118.89	-131.04
149.89	-84.383
189.95	-52.184
240.29	-29.942
273.1	-20.642
300.6	-14.667

Table 5: Results for B using corrected parameters $a_0 = 159.719$, $a_1 = -124.893$, $a_2 = 100.504$

9.2.2 Taylor Series and Lagrange's Interpolation Method (Xenon and Argon)

$Taylor$ is $B^{(n)}(\delta T)^n/n!$								
n is	1	2	3	4	5	6	7	8
T/K	ΔB	ΔB	ΔB	ΔB	ΔB	ΔB	ΔB	ΔB
315.018	-4.3696	-0.68953	-1.32E-01	-3.97E-02	-2.58E-02	-2.37E-02	-2.34E-02	-2.33E-02
273.164	-19.663	-4.4543	-0.96603	-2.36E-01	-1.04E-01	-8.12E-02	-7.70E-02	-7.61E-02
250.024	-35.596	-9.257	-2.0713	-0.4547	-1.44E-01	-8.57E-02	-7.46E-02	-7.23E-02
225.014	-62.218	-18.094	-4.0479	-0.80988	-0.18134	-0.062851	-0.040054	-0.035522
205.147	-93.705	-29.641	-6.6208	-1.2399	-0.19672	-0.0012207	0.03595	0.043213
190.163	-126.36	-42.407	-9.4335	-1.6801	-0.18674	0.090393	0.14246	0.15247

(a) Results of B for Xenon

$Taylor$ is $B^{(n+1)}(\delta T)^n/n!$								
n is	0	1	2	3	4	5	6	7
T/K	ΔB^1	ΔB^1	ΔB^1	ΔB^1	ΔB^1	ΔB^1	ΔB^1	ΔB^1
315.018	2.12E-01	4.87E-02	1.15E-02	3.27E-03	1.73E-03	1.45E-03	1.40E-03	1.39E-03
273.164	5.50E-01	1.63E-01	3.84E-02	7.89E-03	1.65E-03	4.27E-04	1.83E-04	1.34E-04
250.024	0.84464	0.26994	6.15E-02	1.15E-02	1.61E-03	-2.98E-04	-6.69E-04	-7.42E-04
225.014	1.3187	0.47114	0.10648	1.84E-02	1.20E-03	-2.04E-03	-2.64E-03	-2.76E-03
205.147	1.8882	0.72842	0.16252	2.62E-02	0.000047922	-0.0047174	-0.0055895	-0.0057518
190.163	2.504	1.0094	0.22091	3.36E-02	-0.0014691	-0.0077391	-0.0088699	-0.009078

(b) Results of $\Delta B^{(1)}$ for Xenon

Table 6: Results of ΔB as the derivatives of B are increased. $\Delta B^{(n)} = B^{(n)}(square - well) - B^{(n)}(Taylor)$

$Taylor = B^{(n)}(\delta T)^n/n!$								
$n =$	1	2	3	4	5	6	7	8
T/K	ΔB	ΔB	ΔB	ΔB	ΔB	ΔB	ΔB	ΔB
273.1	-0.60434	-0.032759	2.59E-02	3.24E-02	3.30E-02	3.31E-02	3.31E-02	3.31E-02
240.287	-3.537	-0.53881	-0.052231	1.89E-02	2.88E-02	3.03E-02	3.05E-02	3.06E-02
189.95	-16.011	-4.1571	-0.8401	-0.11658	4.04E-02	7.80E-02	8.78E-02	9.03E-02
149.892	-40.437	-14.944	-4.0347	-0.73752	0.22612	0.52565	0.62186	0.65178
118.892	-81.073	-37.749	-11.911	-2.2349	1.006	2.0943	2.4536	2.565
99.589	-129.11	-68.108	-23.388	-4.4386	2.318	4.6347	5.3952	5.6275
90.068	-165.83	-92.033	-32.678	-6.2115	3.3956	6.6883	7.7601	8.0843

(a) Results of B for Argon

$Taylor \text{ is } B^{(n+1)}(\delta T)^n/n!$								
$n \text{ is}$	0	1	2	3	4	5	6	7
T/K	ΔB^1	ΔB^1	ΔB^1	ΔB^1	ΔB^1	ΔB^1	ΔB^1	ΔB^1
273.1	4.91E-02	7.54E-03	1.14E-03	2.08E-04	8.19E-05	6.44E-05	6.20E-05	6.17E-05
240.287	1.36E-01	2.80E-02	5.41E-03	9.07E-04	1.25E-04	-1.57E-05	-4.16E-05	-4.65E-05
189.95	0.39646	0.13639	4.25E-02	9.02E-03	-1.07E-03	-4.32E-03	-5.42E-03	-5.77E-03
149.892	0.89829	0.39097	0.1546	3.13E-02	-1.20E-02	-2.71E-02	-3.22E-02	-3.38E-02
118.892	1.8739	0.92726	0.43366	8.56E-02	-0.046325	-0.092765	-0.10806	-0.1127
99.589	3.278	1.6355	0.83951	1.61E-01	-0.09648	-0.18487	-0.21316	-0.22154
90.068	4.5287	2.1086	1.1441	2.17E-01	-0.13106	-0.24942	-0.28697	-0.298

(b) Results of $\Delta B^{(1)}$ for ArgonTable 7: Results of ΔB as the derivatives of B are increased. $\Delta B^{(n)} = B^{(n)}(square - well) - B^{(n)}(Taylor)$

9.3 Figures

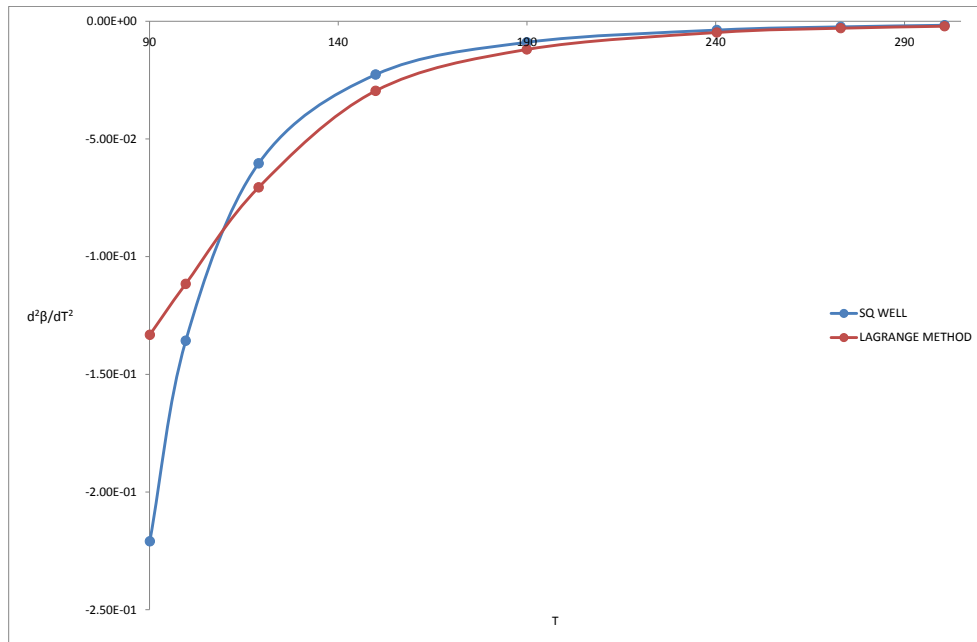
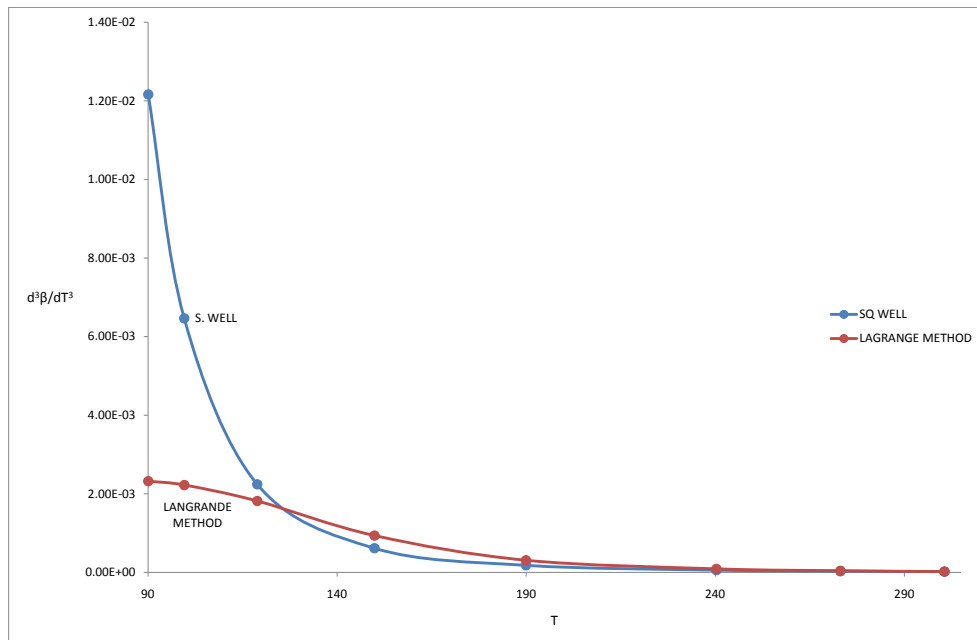
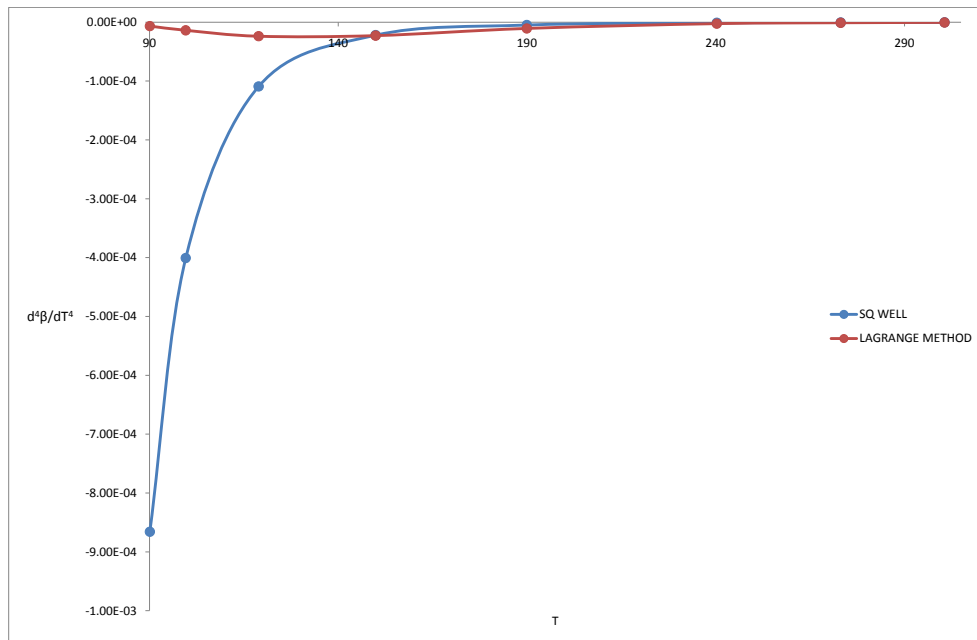
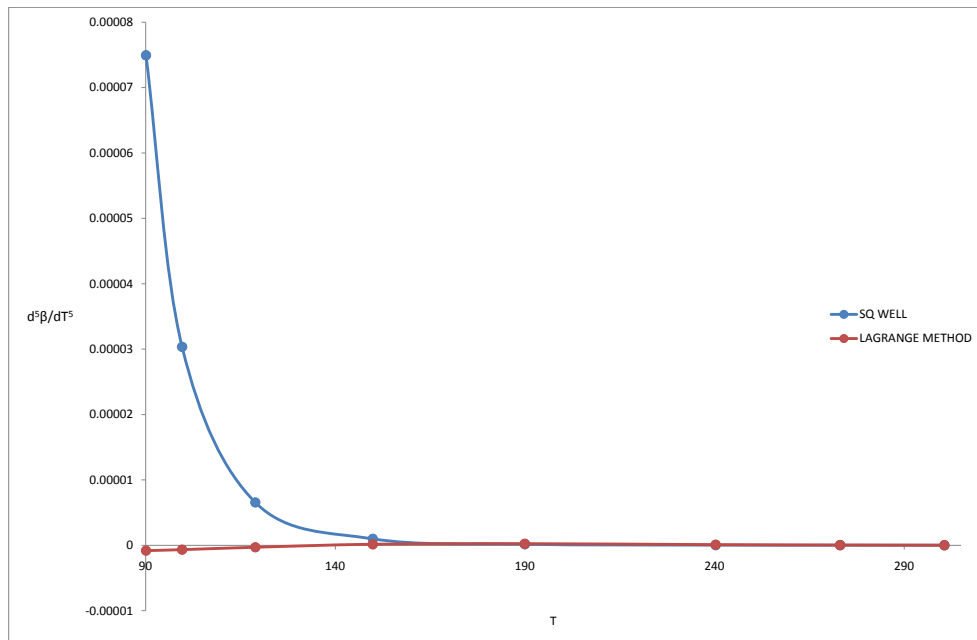


Figure 7: Second derivative of β against T for Argon.

Figure 8: Third derivative of β against T for Argon.

Figure 9: Fourth derivative of β against T for Argon.

Figure 10: Fifth derivative of β against T for Argon.

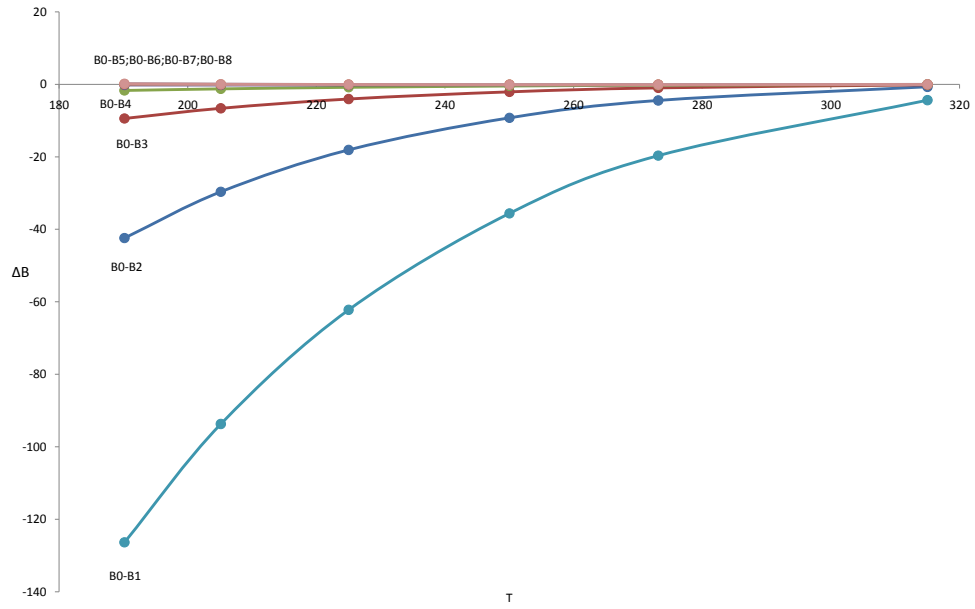


Figure 11: ΔB against Temperature for Xenon. $\Delta B = B(\text{square-well potential}) - B(\text{Taylor})$.

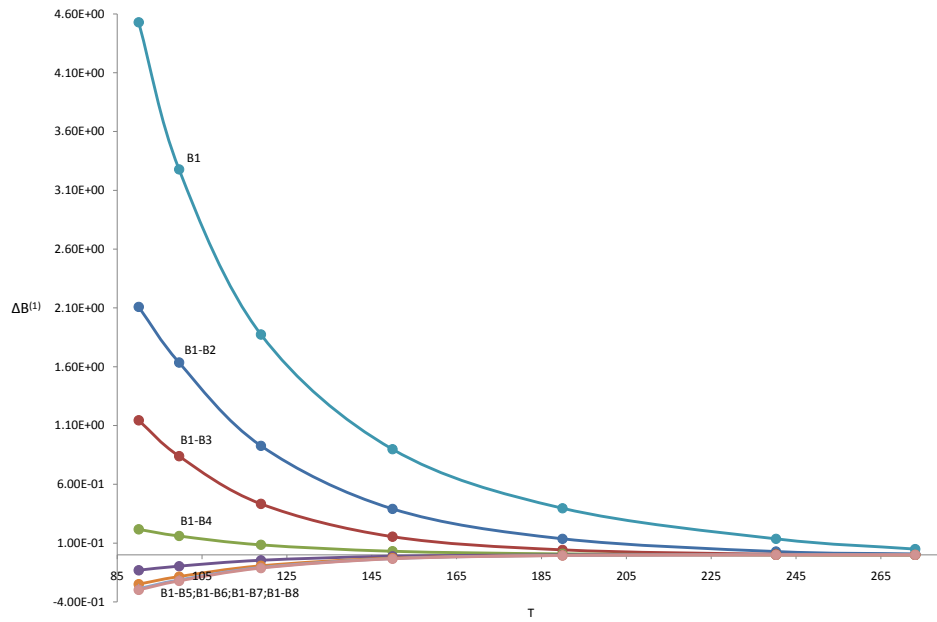


Figure 12: $\Delta B^{(1)}$ against Temperature for Argon. $\Delta B^{(1)} = B^{(1)}(\text{square well potential}) - B^{(1)}(\text{Taylor})$.

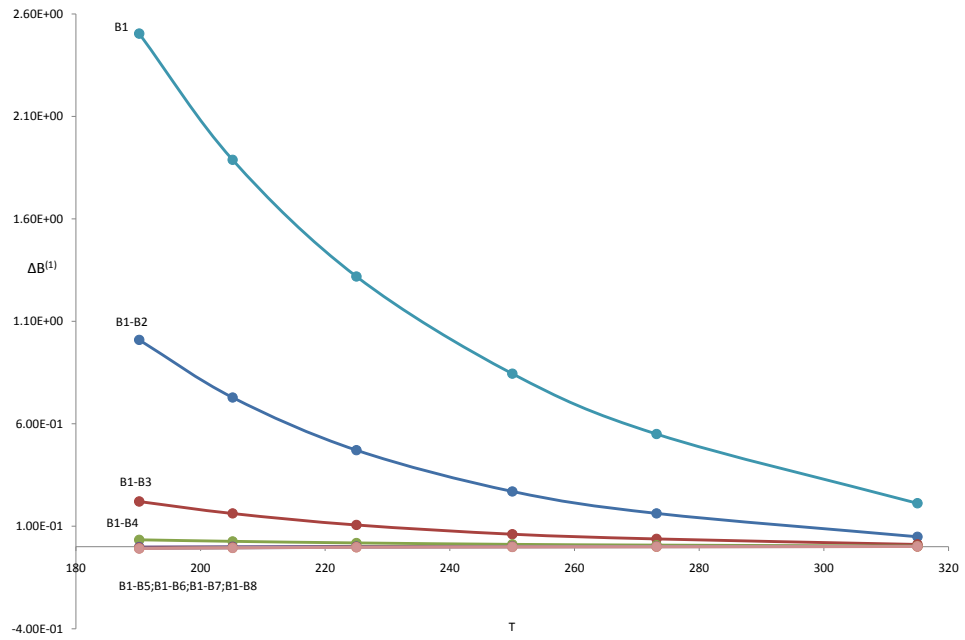


Figure 13: $\Delta B^{(1)}$ against Temperature for Xenon. $\Delta B^{(1)} = B^{(1)}(\text{square} - \text{well potential}) - B^{(1)}(\text{Taylor})$.