

Temperature Variation of Second Virial Coefficient for Deuterium Oxide

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Abstract: The Lennard Jones potential is used to calculate the second virial coefficient for deuterium oxide (D₂O) and use it to obtain Boyle's temperature. It is also use to calculate the viscosity of the deuterium oxide as a function of temperature.

Keywords The Second virial coefficient, Lennard-Jones potential, viscosity, Boyle's temperature T_B.

1. Introduction

The main purpose of this paper is to obtain theoretical values of temperature-dependent second virial coefficient, based upon the Lennard-Jones potential for deuterium oxide. The Lennard-Jones potential as given in (2.1), and use it to obtain a temperature at which the force is exactly cancel. The calculate values of the viscosity as a function of temperature is also based upon the Lennard-Jones parameters.

2. The Second Virial Coefficient

The Lennard-Jones potential is perhaps most common form of potential energy. In equation (1), the first term in the potential is repulsive force term and second term represents the attractive force term [14, 21]. The intermolecular potential energy and the corresponding intermolecular force as L-J (6-12) model are giver by

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

where r is the intermolecular separation, σ is the value of r for which the Lennard-Jones potential φ(r) = 0, ε is the maximum energy of attraction (or depth of the potential wall) which occurs at r = 2^{1/6}σ [19]. A simple expression for the second virial coefficient has been given by

$$B(T) = -2\pi n \int_0^\infty f(r, T) r^2 dr + nh^2 / 24\pi m (kT)^3 \int_0^\infty F^2(r) [f(r, T) + 1] r^2 dr. \quad (2)$$

The first term of the equation is the classical second virial coefficient B(T)_{Classical} and the second term is the correction for quantum second virial coefficient B(T)_{Quantum} or relativistic effect [20, 5, 8, 2]. Therefore we take the numerical values for D₂O from [16] which are $\frac{\epsilon}{k} = 83.4$ (K), σ = 2.75 (Å) for the temperature range (0(K) to 450(K)). Where, the symbols n, r, h, m and k are denoted Avogadro's number or Loschmidt's number, the intermolecular separation. Plank's constant, the molecular mass and Boltzmann constant respectively. The first part in equation (2) is denoted the forces between molecules, that is

$$f(r, T) = \exp\left(-\frac{\phi(r)}{kT}\right) - 1 \quad (3)$$

The intermolecular forces $F(r)$ in equation (2) is related to the intermolecular potential energy $\phi(r)$ [7] may be written as

$$F(r) = -\frac{d}{dr} \phi(r) = \frac{24\epsilon}{\sigma} \left[2 \left(\frac{\sigma}{r} \right)^{13} - \left(\frac{\sigma}{r} \right)^7 \right] \quad (4)$$

where $\phi(r)$ is known as the potential energy of the interaction between two molecules.

2.1. Logic of the temperature, where value of the B(T) is minimum

-Input values $\left(\frac{\epsilon}{k_B}\right)$, σ (Å) and δ in Mathematica programme.

-Input Equation $\text{int}[r_] = ((2\text{Pi} * .602)(1 - e^{-4 * \frac{\epsilon}{k_B} * (\frac{1}{T}) * ((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6)}) * r^2);$ into Mathematica programme

- Calculate minimum value of temperature

For example, numerical evaluation of temperature for D₂O.

$$\frac{\epsilon}{k_B} = 83.4(\text{K}), \sigma = 2.75(\text{Å})$$

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In[1] := int[r_] = ((2Pi * .602)(1 - e^{-4*83.4*(1/T)*((2.75/r)^12 - (2.75/r)^6)}) * r^2);
      B[T_] = Integrate[int[r], {r, 0, ∞}, Assumptions -> {T ∈ Reals, T > 0}]
      FindRoot[B[T] == 0, {T, 1350}]
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Out[2]=

$$\frac{1.372534493879624 \times 10^{26} \sqrt{T} \text{Hypergeometric1F1}[-0.25, 0.5, \frac{83.39999999999999}{T}] - 1.854272583046571 \times 10^{27} \text{Hypergeometric1F1}[0.25, 1.5, \frac{83.39999999999999}{T}]}{T^{3/4}}$$

Out[3]= {T → 285.055}

3. Viscosity

The Chapman-Enskog solution of the Boltzmann equation provided one with a formally complete solution of the problem of interpreting the transport properties of matter. The particular, one obtains phenomenological flow equation to the intermolecular potential function. The viscosity expression (in g/cm sec) for deuterium oxide as a function of temperature [12] is given by

$$\eta \times 10^7 = 266.93 (MT)^{1/2} / \sigma^2 \Omega^{(2,2)*} T^* \quad (5)$$

where M is the molecular weight, T is the absolute temperature, σ is the collision diameter of a molecule in Å and $\Omega^{(2,2)*}$ is the collision integral which is a function of reduced temperature T* [10] is given by

$$\Omega^{(2,2)*} T^* = 1.147 (T^*)^{-0.145} + (T^* + 0.5)^{-2} \quad (6)$$

Where T* is the reduce temperature which is defined as $T^* = k T/\epsilon$ and ϵ is the Lennard-Jones Potential well depth [4]. The Lennard-Jones potential theoretical based curve is shown in figure3 as a function of temperature.

4. Results and discussion

In general, the thermodynamic and transport properties of normal fluids may be expressed in the form of Lennard-Jones (6-12) potential. In this paper, we are focus especially on the Lennard-Jones intermolecular potential for the computations of D₂O properties. The Lennard-Jones potential is a theoretical model to calculate the approximate interaction energy between

molecules. Total potential energy of interaction between two molecules is based upon Lennard-Jones potential function and may be calculated from equation (1) [22]. Thus its formulation fitted curve is shown in fig.1.

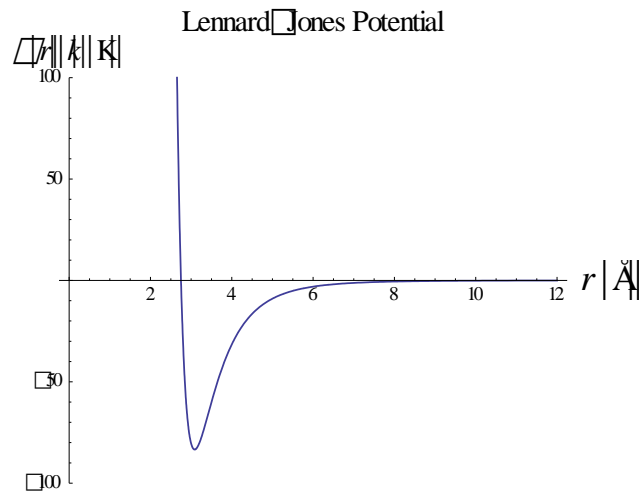


Fig.1. Potential energy $\phi(r)/k$ versus separation $r(\text{\AA})$ for D_2O

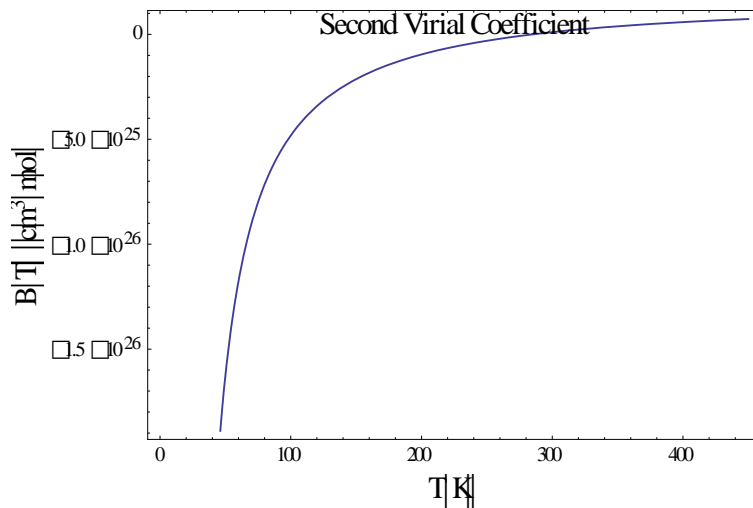
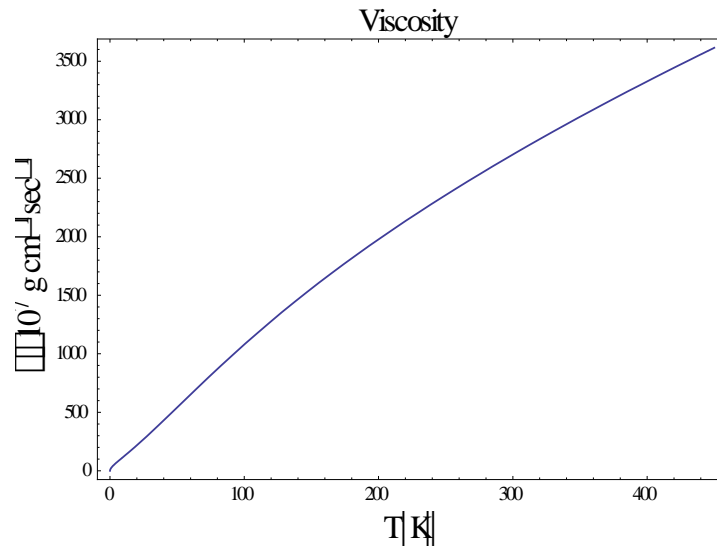


Fig.2. Second virial coefficients $B(T)_{\text{Classical}}$ Verses T (K) for D_2O


 Fig.3. Coefficient of viscosity versus Temperature in (K) for D₂O.

The numerical values of second virial coefficient $B(T)_{\text{Classical}}$ can be carried out by equation (2) as a function of temperature. The Lennard-Jones potential parameters are used to compute the second virial coefficient of D₂O within temperature range (0(K) to 450(K)) which is shown in fig.2. The results of the second virial coefficient $B(T)_{\text{Quantum}}$ is not investigated in this part. A comparison of the calculated and experimental results for deuterium oxide is not present illustrate in this section. There is a large discrepancy at lower temperatures ($T \leq 285.055(\text{K})$), the second virial coefficients $B(T)$ is negative, and where the attractive part of potential for molecules is dominates. However, at high temperature ($T \geq 285.056(\text{K})$), the second virial coefficients $B(T)$ is dominated by the repulsive force and is, consequently positive. A temperature will exist at which the force exactly cancel and $B(T) = 0$; [15] and is known as the Boyle's temperature T_B . At temperature $T = 285.054(\text{K})$, the value of $B(T)$ is $-8.92868 \times 10^{19}(\text{cm}^3/\text{mol})$ and at $T = 285.056(\text{K})$ the value of $B(T)$ is $5.98818 \times 10^{19}(\text{cm}^3/\text{mol})$. The Lennard-Jones parameters are used to calculate the minimum value of $B(T)$ by using the wolfram mathematica 9.0 as follow; $T_B \approx 285.055(\text{K})$, $B(T) \approx -1.47022 \times 10^{19}(\text{cm}^3/\text{mol})$.

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