van der Waals parameters of inert, polar and non-polar gas molecules obtained from atomistic molecular dynamics simulations

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Abstract. A series of atomistic molecular dynamics simulations were performed on the systems of gas molecules within an NVT ensemble, where the number of molecules, the volume and the temperature were controlled. For each simulation, simulated annealing technique was used to gradually vary the temperature and the change in gas pressure was measured within the simulation box at constant volume. Simulation results and regression analysis on the relationships between pressure and temperatures showed that two van der Waals parameters, representing interaction strength and effective size of the gas molecules, depended on shape, size and polarity of the molecules. This study provided an alternative way of demonstrating the basic thermodynamics of gas, and bridging the gap between information from microscopic and macroscopic scales.

1. Introduction

Relationships between thermodynamic parameters of gas molecules are frequently described through the ideal gas equation, \(P V = n R T\) \cite{1}, which is the combination of (i) Boyle’s law, (ii) Charles’ law and (iii) Gay-Lussac’s law. This equation of state is a good approximation for macroscopic parameters of gas systems with low density and weak interactions, which were defined as the ‘Ideal gases’. However, when considering ‘real gas’ with higher density and/or stronger interactions, the ideal gas state equation becomes invalid in most cases. Therefore, a number of empirical models were proposed with more physical details. One of the most commonly known model is \textit{van der Waals model} \cite{2}, in which the total volume is increased due to the specific volume of the gas molecules themselves and vapor pressure is decreased due to the stronger attractive pairwise interactions between gas molecules. Therefore, the equation of state for real gas becomes

\[
P + \frac{an^2}{V^2} (V - nb) = nRT,
\]

where \(P, V\) and \(T\) represents pressure, volume and temperature, respectively. \(n\) represents total number of moles, while \(a\) and \(b\) are the \textit{van der Waals coefficients}. The coefficient \(a\) can be interpreted as the contribution of intermolecular attractive forces to the vapor pressure, in which the product between \(a\) and the collision probability (~square concentration \(n^2/V^2\)) is proportional to the reduced pressure and the correction \(an^2/V^2\) is needed in order to match the vapor pressure to that of ideal gas. The coefficient \(b\) can then be interpreted as the specific volume per mole of gas molecules adding up the total volume.
V' and the correction $nb$ is needed in order to match the volume unoccupied by gas molecules to that of the ideal gas. For a closed system at constant volume, equation (1) can be rearranged as

$$P = -\left(\frac{an^2}{V^2}\right) + \left(\frac{nR}{V - nb}\right)T;$$

therefore equation (1) is valid if pressure is linearly proportional to temperature, where coefficients $a$ and $b$ can be defined. An alternative method to examine the validity of the van der Waals equation and estimate the coefficients $a$ and $b$ is to use the atomistic molecular dynamics simulations. With the predefined forcefield parameters [3] for each type of atoms, potential energy functions consisting bonding and non-bonding interactions were estimated. Then, the collective behaviours of molecules can be monitored from the resulting Newtonian motion from those potentials and the resulting kinetics from the assigned temperature. Numerically solving Newtonian equations of motion for all atoms in the systems provides the trajectory file containing coordinates and velocities of all atoms at a given time, and macroscopic parameters, e.g. pressure, can be calculated. In this work, we performed simulated annealing atomistic molecular dynamics (MD) simulations, in which temperatures were varied and pressures were calculated as functions of temperatures for four simple molecules: 1) helium (representing inert gases), 2) water (representing highly-polar molecules), 3) methanol (representing intermediate-polar molecules) and 4) methane (representing non-polar molecules). Changes in molecular configurations can be visualized from MD trajectories at varied temperature.

2. Methodology

2.1. Simulation setup

Atomic coordinates of all molecules were obtained from the PUBCHEM database [4]. Density functional theory (DFT) calculation with 6-31G* basis set [5] and Chachiyo correlation [6] was performed for the three dimensional structure of each molecule by using the Siam Quantum software, so that the partial charge distribution data and total electric dipole moment was obtained (see figure 1). Then, the partial charges were assigned to the OPLS/AA molecular mechanics forcefield parameters where covalent and van der Waals terms for each type of atoms were already defined [3]. After that, for each molecule type, a $10 \times 10 \times 10$ nm$^3$ simulation box was built and atomistic coordinates for the center of mass of 1000 molecules (1.66 molar) were assigned. Energy minimization using steepest descent algorithm was performed for each system followed by a 1000 ps simulated annealing MD simulation using GROMACS 5.1.2 program [7], in which the temperature increased linearly from 0 to 1000 K, in which LINCS [8] holonomic constraints, v-rescale thermostat [9] and Berendsen baro-stat [10] were applied with 1.0 ps time constants.

![Figure 1](image_url)

**Figure 1.** Equi-density surface of three dimensional structures along with the partial charges of a) helium, b) methane, c) water and d) methanol.
2.2. Trajectory analysis

Pressure at a given temperature can be calculated from an alternative definition derived from virial theorem [1]:

$$P = \frac{1}{V} \left[ N k_B T - \frac{1}{3} \sum_{i<j}^{N} \sum_{i}^{N} r_{ij} F_{ij} \right],$$  \hspace{1cm} (3)

where $N$ is the total number of atoms, $r_{ij}$ and $F_{ij}$ are the distance and magnitude force between pairs of atoms $i$ and $j$. Then, for each type of molecule, pressure from each simulation snapshot was plotted as functions of temperature. Then van der Waals coefficients $a$ and $b$ were obtained from linear regression of a chosen temperature range displaying linear pressure increasing.

3. Results

A series of atomistic MD simulations of helium, methane, water and methanol molecules were performed under an NVT ensemble at temperatures varied from 0 K to 1000 K by simulated annealing techniques. During the simulations, helium and methane mostly remained in gaseous phase due to their low boiling-point temperatures. However, liquid-gas transition can be seen for water and methanol during the courses of simulations (see figure 2a and figure 2b).

![Figure 2. Atomic coordinates of a) water molecules at 200, 400, 600 and 800 K and b) methanol molecules at 200, 400, 600 and 800 K.](image)

The P-T relationship in figure 3 shows that, pressure rapidly increased with temperature for helium and methane (see figure 3a and figure 3b), even at low temperatures. Similar behavior of inert gas was also observed from another study by Sweet et al. [11]. However, for water and methanol, pressure increased slowly at low temperature, corresponding to the condensed phases (liquid and/or solid) shown in figure 2. As the temperature of water and methanol systems approached their boiling points, abrupt changes in pressure were observed along with their transitions into gaseous phases (see figure 3c and figure 3d). Simulated annealing atomistic molecular dynamics (MD) simulations from zero to 800-1000 K were performed for helium, water, methanol and methane at 1 molecule/nm$^3$ or 1.66 mol/litre molar ratio. Van der Waals coefficients $a$ and $b$ were extracted from each simulation trajectory (see
The coefficient $a$, representing attractive interactions, of the highly-polar water molecules was the highest, while the coefficients $a$ were low for methane and helium. The coefficient $b$, representing specific volume occupied by gas molecules, was the lowest for the smallest helium molecule and the predicted effective van der Waals radius of 0.16 nm was found very close to the standard value 0.14 nm. However, large systematic error was found for the coefficients $b$ of other molecules. The error could come from finite number of sample molecules and high molar ratios. The van der Waals parameters of inert gases can be validated with the experiments and previous simulation results [11] and the effects of polarity were addressed by our simulations.

Table 1. Mass, electric dipole moment, van der Waals parameters and effective van der Waals radii of the four molecules in this study.

| Molecule      | Mass (g/mol) | Electric Dipole (C m) | $a$ (J m$^3$/mol$^3$) | $b$ (m$^3$/mol) | $r$ (Å) |
|---------------|--------------|-----------------------|------------------------|----------------|--------|
| Helium(He)    | 4.0026       | 0.0000                | 1.054×10$^{-2}$        | 0.104×10$^{-4}$ | 1.604  |
| Methane(CH$_4$)| 16.0400     | 0.0000                | 14.93×10$^{-2}$       | 2.778×10$^{-4}$ | 4.794  |
| Water(H$_2$O) | 18.0153      | 2.4596                | 143.7×10$^{-2}$       | 1.088×10$^{-4}$ | 3.507  |
| Methanol(CH$_3$OH) | 32.0400 | 2.1502               | 117.2×10$^{-2}$       | 1.251×10$^{-4}$ | 3.675  |

Figure 3. Pressure calculated from equation (3) as functions of temperatures for simulated annealing simulations of (a) helium, (b) methane, (c) water and (d) methanol. Red lines represented the linear relationships of $P$-$T$ in equation (2) and green dashed lines represented simulated boiling-point temperature under at concentration 1.66 molar.
4. Conclusion
Microscopic details of molecular motions from MD trajectories and macroscopic parameters from van der Waals coefficients evaluated from the simulation results can serve as a great example for students in statistical thermodynamics and MD simulations classes, as melting and boiling at molecular level can be visualized with high accuracy. These preliminary results could also be a good starting point for further MD studies with better equilibrated trajectories, larger number of samples and simulation boxes, which consume significantly larger computing time.

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References
[1] Landau L D and Lifshitz E M 1980 Statistical Physics (Oxford: Elsevier)
[2] Andrews T 1869 Phil. Trans. R. Soc. Lond. 159 575–90
[3] Robertson M J, Tirado-Rives J and Jorgensen W L 2015 J. Chem. Theory Comput. 11 3499–509
[4] Kim S et al 2019 Nucleic Acids Res. 47 D1102–9
[5] Ditchfield R, Hehre W J and Pople J A 1971 J. Chem. Phys. 54 724–8
[6] Chachiyo T 2016 J. Chem. Phys. 145 021101
[7] Abraham M J, Murtola T, Schulz R, Pall S, Smith J C, Hess B and Lindahl E 2015 SoftwareX 1–2 19–25
[8] Hess B et al 1997 J. Comput. Chem. 18 1463–1472
[9] Bussi G, Donadio D and Parrinello M 2007 J. Chem. Phys. 126 014101
[10] Berendsen H J C, Postma J P M, van Gunsteren W F, DiNola A and Haak J R 1984 J. Chem. Phys. 81 3684–90
[11] Sweet C, Akinfenwa O and Foley J J 2018 J. Chem. Educ. 95 384–92