Derivation of Van der Waal’s equation of state in microcanonical ensemble formulation

Aravind P. Babu, Kiran S. Kumar and M. Ponmurugan*
Department of Physics, School of Basic and Applied Sciences, Central University of Tamilnadu, Thiruvarur 610 005, Tamilnadu, India.

February 7, 2018

Abstract

The Van der Waal’s equation of state for a (slightly) non-ideal classical gas is usually derived in the context of classical statistical mechanics by using the canonical ensemble. We use the hard sphere potential with no short range interaction and derive Van der Waal’s equation of state in microcanonical ensemble formulation.

1 Introduction

The ensemble theory of equilibrium statistical mechanics connects the macroscopic relations of thermodynamic systems and its microscopic constituents [1, 2, 3]. An ensemble of a given thermodynamic system is a set of distinct microstates with appropriately assigned probability for a fixed macrostate [1]. In a macrostate of fixed energy $E$, volume $V$ and the number of particle $N$ and all its microstates are equiprobable then such an ensemble is called as microcanonical ensemble [3].

The most important concept in statistical mechanics theory is the equivalence of ensemble, that is, the ensemble theory should provide the same macroscopic relations in the thermodynamic limit of infinite size irrespective of the chosen ensemble. This concept of ensemble equivalence has been
verified easily by incorporating different ensemble approach to simple system known as ideal gas. Whatever the ensemble one may choose, we can finally obtain the ideal gas equation of state as $PV = nRT$ \[^{[2],[5]}\], where $P$ is the pressure, $V$ is the volume, $T$ is the temperature of the system, $n$ is the number of moles and $R$ is the universal gas constant.

An ideal gas is the simplest thermodynamic system in which there is no intermolecular interactions. By considering the intermolecular interactions, Van der Waals proposed the equation of state for a real gas which is given by \[^{[6]}\]

$$
(P + \frac{n^2a}{V^2})(V - nb) = nRT,
$$

where $a$ and $b$ are the Van der Waal’s constants. The derivation of Van der Waal’s equation of state has been found in most of the Statistical Physics books which are in canonical ensemble formulation \[^{[7]}\]. To our knowledge, there is no such study available in the literature for any other ensemble formulation, in particular, microcanonical ensemble formulation. In this paper, we use the hard sphere potential approximation and derive the Van der Waal’s equation of state in microcanonical ensemble formulation.

## 2 Hamiltonian for Van der Waal’s gas

Consider a monoatomic non ideal gas of $N$ particles having identical mass $m$ in a container of fixed volume $V$ at temperature $T$. In order to treat the problem in classical statistical mechanics, we assume that the temperature is taken to be sufficiently high and the density $\rho = \frac{N}{V}$ is sufficiently low. The total energy (Hamiltonian) of the system is $H = K + U$, where $K = \frac{1}{2m} \sum_{l=1}^{3N} p_l^2$ is the kinetic energy of the gas of $3N$ degrees of freedom moving with momentum $p_l$. $U$ is the total potential energy due to the interaction that exists between the molecules. In semi-classical approximation, we consider the molecules to be hard spheres of radius $r_0$, so that the distance between the two molecules can come close to $r_0$ \[^{[2]}\]. The interaction between a pair of molecules $i$ and $j$ separated by the intermolecular distance $r$ is given by the hard sphere potential with no short range interaction as \[^{[7],[8]}\]

$$
u(r) = -u_0 \left(\frac{r_0}{r}\right)^6 \text{ for } r \geq r_0,
$$

2
where $u_0$ is the depth of the potential. The total potential energy is given by the sum of interactions between the pair of all molecules as

$$U = \frac{1}{2} \sum_{i=1}^{N} u_i,$$  \hspace{1cm} (3)

where $u_i$ is the interaction energy of $i^{th}$ molecule with all other molecules in the specified region given in spherical polar coordinates as

$$u_i = \int_{r_0}^{\infty} \int_{0}^{2\pi} \int_{0}^{\pi} \rho u(r) r^2 \sin \theta \ dr d\theta d\phi$$ \hspace{1cm} (4)

$$u_i = -4\pi \frac{Nu_0}{V} \int_{r_0}^{\infty} \frac{r^6}{r^4} dr = -\frac{4\pi Nu_0 r_0^3}{3V}. \hspace{1cm} (5)$$

Here, we assume that the density ($\rho = \frac{N}{V}$) of the gas to be uniform throughout the volume. Thus, the total potential energy is given by

$$U = \frac{1}{2} Nu_i = -a'\frac{N^2}{V}, \hspace{1cm} (6)$$

where $a' = \frac{2\pi u_0 r_0^3}{3}$. Therefore the total Hamiltonian is given by

$$H = \sum_{l=1}^{3N} \frac{p_l^2}{2m} - \frac{a'N^2}{V} \equiv E. \hspace{1cm} (7)$$

3 Microcanonical entropy and equation of state for Van der Waal’s gas

Because of the hard sphere approximation, there should be a correction in the total volume of the Van der Waal’s gas. By considering the molecules as a hard sphere of diameter $2r_0$, the center of each molecules excluded by other molecule by a volume which is equivalent to the volume of sphere of radius $2r_0$ is known as the excluded volume. The excluded volume for the two molecules of radius $r_0$ is $\frac{4}{3}\pi (2r_0)^3$. Since the system contains N molecules, the excluded volume $v$ for $N$ molecule can be obtained as $v = Nb'$ where $b' = \frac{2\pi (2r_0)^3}{3}$. The corrected volume which is available for the gas molecules in the container is given by

$$V' = V - Nb'. \hspace{1cm} (8)$$
Consider a small volume in phase space, the total number of microstates available for the system in microcanonical ensemble of fixed $E, V$ and $N$ of Eq.(7) is given by \[2, 3, 6\]

$$\Omega(E, V, N) = \frac{1}{N!h^{3N}} \frac{\partial \omega}{\partial E}, \tag{9}$$

where $h$ is the Planck’s constant and the volume integral \[5, 6, 9\]

$$\omega(E, V, N) = \int \int_{H(q,p) \leq E} d^{3N}q \, d^{3N}p. \tag{10}$$

For hard sphere potential, the above integral can be written as

$$\omega(E, V, N) = (V-Nb')^N \int_{H(q,p) \leq E} d^{3N}p, \tag{11}$$

where $\int_{H(q,p) \leq E} d^{3N}q = (V')^N = (V-Nb')^N$ for Van der Waal’s gas and Eq.(7) can be rearranged as

$$\sum_{i=1}^{3N} p_i^2 = 2m \left( E + \frac{a'N^2}{V} \right) \tag{12}$$

The integral in Eq.(11) is just the volume of a $3N$ dimensional sphere of radius $R = \sqrt{2m(E + \frac{a'N^2}{V})}$ which can be obtained as (see appendix) \[2, 3\]

$$\omega(E, V, N) = \frac{\pi^{3N/2}}{\frac{3N}{2} \Gamma\left(\frac{3N}{2}\right)} (V-Nb')^N R^{3N} \tag{13}$$

$$= \frac{\pi^{3N/2}}{\frac{3N}{2} \Gamma\left(\frac{3N}{2}\right)} (V-Nb')^N \left[ 2m \left( E + \frac{a'N^2}{V} \right) \right]^{3N/2} \tag{14}$$

Using the above equation we can calculate the number of microstates as in Eq.(9) for Van der Waal’s gas in micro canonical ensemble as

$$\Omega(E, V, N) = \frac{1}{N!h^{3N}} \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (V-Nb')^N (2m)^{3N/2} \left( E + \frac{a'N^2}{V} \right)^{\frac{3N}{2}-1}. \tag{15}$$

For large $N$, we can approximate $\frac{3N}{2}-1 \simeq 3N/2$ and $\Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2}-1\right)! \simeq \frac{3N}{2}!$

then

$$\Omega(E, V, N) = \frac{1}{N!h^{3N}} \frac{\pi^{3N/2}}{\frac{3N}{2} \Gamma\left(\frac{3N}{2}\right)} (V-Nb')^N (2m)^{3N/2} \left( E + \frac{a'N^2}{V} \right)^{\frac{3N}{2}}. \tag{16}$$
The Boltzmann microcanonical entropy of the system is given by [2, 5, 6],

\[ S(E, V, N) = k_B \ln \Omega(E, V, N). \]  

(17)

Using Eq.(16) and applying Stirling approximation \( \ln N! = N \ln N - N \), we can obtain the microcanonical entropy of Van der Waal’s gas is

\[ S(E, V, N) = k_B N \left\{ \frac{5}{2} + \ln \left( \frac{V - Nb'}{N} \right) \left[ \frac{4\pi m}{3Nh^2} \left( \frac{E + a'N^2}{V} \right) \right]^{\frac{3}{2}} \right\}. \]  

(18)

At constant \( V \) and \( N \), from the Maxwell’s First thermodynamic relation \( dE = TdS - pdV \), we get [11 5]

\[ \frac{\partial S}{\partial E} = \frac{1}{T} \] 

(19)

\[ \frac{\partial S}{\partial V} = P \] 

(20)

Using Eq.(18), we obtain

\[ \frac{1}{T} = \frac{3}{2} Nk_B \left( E + \frac{a'N^2}{V} \right)^{-1} \] 

(21)

The above equation can be rearranged in terms of energy as

\[ E = \frac{3}{2} Nk_B T - \frac{a'N^2}{V} \] 

(22)

Using Eq.(18) and Eq.(22), one can get

\[ \frac{P}{T} = \frac{Nk_B}{(V - Nb')} - \frac{a'N^2}{V^2T}. \]  

(23)

\[ \left( P + \frac{a'N^2}{V^2} \right)(V - Nb') = Nk_B T \] 

(24)

Substitute \( N = nN_a \), \( a = a'N_a^2 \), \( b = b'N_a \) and \( k_B N_a = R \) in the above equation, we get

\[ \left( P + \frac{n^2a}{V^2} \right)(V - nb) = nRT. \] 

(25)

where \( R \) is gas constant, \( n \) is the number of moles and \( N_a \) is the Avogadro’s number. Thus, we have obtained Van der Waal’s equation of state with Van der Waal’s constants \( a \) and \( b \).
4 Conclusion

We used the hard sphere potential and derived Van der Waal’s equation of state in microcanonical ensemble formulation. Even though the canonical ensemble is much easier to use in actual application than the microcanonical ensemble, one should not ruled out the various studies of the same system in other ensemble formulation. In this context, our result also verified the equivalence of ensemble for Van der Waal’s gas.

Appendix

The integral in Eq. (11) can be considered as the volume of 3N dimensional spheres of radius $R = \sqrt{2m(E + \frac{\Delta N^2}{M})}$ which is given by [5, 6]

\[ V_N(R) = \int_{\sum_{l=1}^{3N} y_l^2 \leq R^2} d^{3N} p \]
\[ = R^{3N} \int_{\sum_{l=1}^{3N} y_l^2 \leq 1} d^{3N} y \]
\[ = R^{3N} C_{3N}, \] (28)

where $y_l = p_l / R$, $C_{3N} = \int_{\sum_{l=1}^{3N} y_l^2 \leq 1} d^{3N} y$ and

\[ d^{3N} y = dV_N(R) = 3NC_{3N} R^{3N-1} dR \] (29)

Using the identity $\int_{-\infty}^{+\infty} e^{-y^2} dy = \sqrt{\pi}$ and Eq. (29), we consider the integral

\[ \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} e^{-(y_1^2 + y_2^2 + \cdots + y_{3N}^2)} d^{3N} y = \pi^{3N/2} \] (30)

and transform it in to polar coordinates as,

\[ 3NC_{3N} \int_{0}^{\infty} R^{3N-1} e^{-R^2} dR = \pi^{3N/2}. \] (31)

Substituting $R^2 = x$, we obtain

\[ C_{3N} = \frac{\pi^{3N/2}}{\frac{3N}{2} \Gamma\left(\frac{3N}{2}\right)} \] (32)
where the Gamma function
\[ \Gamma\left(\frac{3N}{2}\right) = \int_0^\infty x^{\frac{3N}{2}-1} e^{-x} dx. \] (33)

Therefore, Eq.(11) becomes
\[
\omega(E, V, N) = \frac{\pi^{3N/2}}{\frac{3N}{2} \Gamma\left(\frac{3N}{2}\right)} (V - Nb')^N R^{3N} \]
\[
= \frac{\pi^{3N/2}}{\frac{3N}{2} \Gamma\left(\frac{3N}{2}\right)} (V - Nb')^N \left[ 2m \left( E + \frac{a'N^2}{V} \right) \right]^{3N/2} \] (35)

Acknowledgements  I would like to thank N. Barani Balan for proof reading the manuscript.

e-mail correspondence: ponphy@cutn.ac.in

References

[1] H. Callen, *Thermodynamics and an introduction to thermostatistics* (Wiley, New York, 1985).

[2] R. K. Pathria, *Statistical Mechanics* (Pergamon Press, New York, 1985).

[3] K. Huang, *Statistical Mechanics* (Wiley, New York, 1987).

[4] K. P. N. Murthy, *Monte Carlo Methods in Statistical Physics* (University Press, Hyderabad, India, 2004).

[5] K. P. N. Murthy, *Excursions in Thermodynamics and Statistical Mechanics* (University Press, Hyderabad, India, 2009).

[6] F. W. Sears, and G. L. Salinger, *Thermodynamics, Kinetic Theory, and statistical Thermodynamics* (Addison-Wesley, Philippines, 1975).

[7] F. Reif, *Fundamentals of Statistical and Thermal Physics* (Waveland press, Long Grove, Illinois, 2009).
[8] M. P. Allen and D. J. Tildesley, *Computer simulation of liquids* (Clarendon Press, Oxford, 2009).

[9] W. Greiner, L. Neise and H. Stocker, *Thermodynamics and Statistical mechanics* (Springer, New York, 1995).