

Non ideal gas in Micro Canonical Ensemble



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Abstract

In the case of real gases, the interaction among the constituent particles govern the physical and chemical properties of the system. Thermodynamics of real system are obtained in canonical ensemble using different potentials and by using mean field approximations. Here we use square well potential and generalized hard sphere Lennard Jones potential to obtain the non-ideal equation of state and thermodynamic properties of a non-ideal system using micro canonical ensemble.

Keywords: Micro Canonical Ensemble, Equation of state, Non ideal gas.

Resumen

En el caso de los gases reales, la interacción entre las partículas constituyentes gobierna las propiedades físicas y químicas del sistema. La termodinámica del sistema real se obtiene en conjunto canónico utilizando diferentes potenciales y utilizando aproximaciones de campo medio. Aquí utilizamos el potencial de pozo cuadrado y el potencial de Lennard Jones de esfera dura generalizada para obtener la ecuación de estado no ideal y las propiedades termodinámicas de un sistema no ideal utilizando un conjunto microcanónico.

Palabras clave: Conjunto micro canónico, ecuación de estado, gas no ideal.

I. INTRODUCTION

When density is very low, gases obey ideal gas equation of state, $PV = NkT$, where P is the pressure, V is the volume, N is the total number of particles, k is Boltzman's constant and T is the temperature. When there is no inter particle interactions this equation of state can be obtained from the usual statistical ensemble formalism [1, 2, 3, 4, 5]. When the temperature is low and density is high, due to the inter particle interactions, the equation of state starts to deviate from the ideal behavior and forms non ideal equation of state which can be written as a virial series.

$$P = nkT[1 + Bn + Cn^2 + \dots], \quad (1)$$

where n is the number density and B, C etc. are the virial coefficients [1, 2, 3, 4, 5]. The first non-ideal equation of state derived by considering the molecular interactions is the van der Waals model [6, 7], which can be used to explain phase transition and to find out the critical parameters. Here we use two types of inter particle potentials to derive non ideal equation of state in micro canonical ensemble. The potentials used are, the square well potential model defined as

$$\begin{aligned} u(r) &= \infty; r < \sigma, \\ u(r) &= -\epsilon; \sigma < r < \lambda\sigma, \end{aligned} \quad (2)$$

and generalized hard sphere Lennard Jones potential given by,

$$\begin{aligned} u(r) &= \infty; r < \sigma, \\ u(r) &= -\epsilon \left(\frac{\sigma}{r}\right)^n; r \geq \sigma; n > 3, \end{aligned} \quad (3)$$

where σ is the hard-core radius, the region σ to $\lambda\sigma$ is the region of attractive potential, λ is the parameter deciding the dimension of the well and ϵ represents the strength of the attractive potential [8].

II.METHODOLOGY

To study the properties of real gases using the interaction potential, different methods are used in canonical and grand canonical ensemble like mean field treatment and cluster expansion method [9]. But the calculation of configuration integral is difficult even with simple potentials. Here we use the microcanonical ensemble which ensures the main requirement like additivity of entropy. The weak interaction in the system is essential for keeping the ergodic principle and the system cannot form an equilibrium state without transferring energy between particles. When the system is dilute, the motion of any pair of molecules is not influenced by the other particles. So here we take the total potential

energy as the sum of potential energies between the pair of all molecules by taking examples of two potentials from Eq. (1) and Eq. (2), and obtain the thermodynamics in the microcanonical ensemble. So, with the interaction potential energy we calculated the available phase space volume and then the number of microstates in order to derive the equation of state. Square well potential is used when the attractive interactions in gaseous systems and Lennard Jones potential is widely used as inter particle potential for neutral particle systems. Considering a low-density system of particles with mass m and momentum p , the Hamiltonian can be written as the sum of kinetic and potential energies of particles in $3N$ degrees of freedom [1, 2, 3, 4]

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U. \quad (4)$$

For calculating the total potential energy U , we take sum of interaction energy between pair of all molecules and we denote u_i as the potential energy of interaction of i^{th} particle with all other particles in the given volume which gives the correct potential energy.

$$U = \frac{1}{2} \sum_{i=1}^N u_i. \quad (5)$$

The factor $\frac{1}{2}$ take care of the doubling of potential energy terms between any pair of molecules.

III. POTENTIAL ENERGY USING SQUARE WELL POTENTIAL

Assuming uniform density of particles and using the spherical polar coordinates, the potential energy of first particle with all other particles in the system is given by,

$$u_i = \int_{\sigma}^{\sigma\lambda} \int_0^{2\pi} \int_0^{\pi} \rho u(r) r^2 \sin\theta \, dr \, d\theta \, d\phi, \quad (6)$$

$$u_i = \frac{4\pi N}{V} \int_{\sigma}^{\lambda\sigma} -\epsilon r^2 \, dr, \quad (7)$$

$$u_i = \frac{-4\pi N \epsilon}{3V} [\sigma^3(\lambda^3 - 1)]. \quad (8)$$

The total potential energy is given by

$$U = \frac{-4\pi N^2 \epsilon}{6V} [\sigma^3(\lambda^3 - 1)]. \quad (9)$$

This can be written as

$$U = -a_1 \frac{N^2}{V}, \quad (10)$$

where the constant a_1 is given by

$$a_1 = \frac{2\pi\epsilon}{3} [\sigma^3(\lambda^3 - 1)]. \quad (11)$$

IV. POTENTIAL ENERGY USING GENERALIZED HARD SPHERE LENNARD JONES POTENTIAL.

Using the potential defined in Eq. (2), we can calculate the u_i by using Eq. (6).

$$u_i = \frac{4\pi N}{V} \int_{\sigma}^{\infty} -\epsilon \left(\frac{\sigma}{r}\right)^n r^2 \, dr, \quad (12)$$

$$u_i = \frac{4\pi N \epsilon}{V} \left[\frac{\sigma^3}{3-n} \right]. \quad (13)$$

The total potential energy is given by

$$U = \frac{-2\pi\epsilon\sigma^3 N^2}{(n-3)V}, \quad (14)$$

$$U = -a_2 \frac{N^2}{V}, \quad (15)$$

where $a_2 = \frac{2\pi\epsilon\sigma^3}{(n-3)}$.

We see that for both potentials the potential energy can be written in a common form taking a as general representation for a_1 and a_2 . Then, the total energy is given by

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + -a \frac{N^2}{V}. \quad (16)$$

V. CALCULATION OF NUMBER OF MICRO STATES

Since in this analysis we used the hard-core repulsive potential, two particles cannot come closer than the diameter of the molecule $d = 2\sigma$. If the system contains N particles the corrected volume V' is given by difference between actual physical volume and excluded volume with $b = \frac{2\pi d^3}{3}$.

$$V' = V - Nb. \quad (17)$$

The total number of micro states can be calculated by finding out the total phase space volume,

$$\Omega = \frac{\text{Total phase space volume}}{N!h^{3N}}, \quad (18)$$

$$\Omega = \frac{(V-Nb)^N V_p}{N!h^{3N}}, \quad (19)$$

where $(V - Nb)^N$ is the spatial volume available for N particles, V_p is the volume of $3N$ dimensional momentum sphere and $N!$ is used as the Gibb's correction factor. The volume of $3N$ dimensional sphere is given by [3, 4],

$$V_{3N} = \frac{\pi^{\frac{3N}{2}} R^{3N}}{\left(\frac{3N}{2}\right)!}. \quad (20)$$

The radius R of the momentum sphere can be found out from the total energy E from Eq. (16).

$$R = \sqrt{2m \left(E + \frac{aN^2}{V} \right)}. \quad (21)$$

Then the total number of micro states can be calculated as

$$\Omega = \frac{(V - Nb)^N \pi^{\frac{3N}{2}} \left[2m \left(E + \frac{aN^2}{V} \right) \right]^{\frac{3N}{2}}}{N! h^{3N} \left(\frac{3N}{2} \right)!}. \quad (22)$$

Using Boltzman's equation for entropy $S = k \ln \Omega$

$$S = \frac{5}{2} Nk + Nk \ln \left[\left(\frac{V - Nb}{N} \right) \left(\frac{4\pi m}{3Nh^2} \right) \left(E + \frac{aN^2}{V} \right)^{\frac{3}{2}} \right]. \quad (23)$$

Using the first law of thermodynamics the thermodynamic properties can be calculated.

$$TdS = dE + PdV - \mu dN. \quad (24)$$

Internal energy is obtained from

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T}, \quad (25)$$

$$\frac{1}{T} = \frac{3}{2} Nk \left(E + \frac{aN^2}{V} \right)^{-1}. \quad (26)$$

Rearranging

$$E = \frac{3}{2} NkT - a \frac{N^2}{V}. \quad (27)$$

The internal energy shows deviation from the ideal value. The non-ideal equation of state can be found out from

$$\left(\frac{\partial S}{\partial V} \right)_{N,E} = \frac{P}{T}. \quad (28)$$

With the use of the calculated value of internal energy, we get

$$\frac{P}{T} = \frac{Nk}{V - Nb} - a \frac{N^2}{V^2 T}. \quad (29)$$

Hence we get

$$\left(P + \frac{aN^2}{V^2} \right) (V - Nb) = NkT. \quad (30)$$

This equation of state is similar to van der Waals equation of state with coefficient a as $a_1 = \frac{2\pi\epsilon}{3} [\sigma^3(\lambda^3 - 1)]$ for the square well potential and $a_2 = \frac{2\pi\epsilon\sigma^3}{(n-3)}$ for the generalized hard sphere Lennard Jones potential.

VI. CONCLUSION

Studying thermodynamic properties and equation of state of different physical systems was a subject of interest of all time. Here we discussed a method for obtaining non ideal equation of state by considering two body interaction potentials like square well potential and generalized hard sphere Lennard Jones potential using micro canonical ensemble.

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