Thermodynamics of Dipolar Hard Sphere System

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Abstract

The thermodynamic properties of real physical systems are greatly influenced by the inter particle interactions. Recent experimental progress in trapping and cooling of molecular gases creates great interest in the study of gases with dominant dipole-dipole interactions with electric or magnetic dipole moments. In this paper we use mean field method to find out the non ideal equation of state and thermodynamic properties of a dipolar system.

Indexing terms/Keywords: Equation of state, Polar systems, Mean field Theory

1.   Introduction

In statistical mechanics, the study of real systems with interactions are always an interesting research topic. Real systems are usually modelled by interaction potential models of different types [1,2,3,4,5]. The use of Mayer cluster expansion was one major way to study interacting systems [1]. The high density equation of state and condensation of gases with Lennard-Jones potential was studied recently by Ushcats [6,7] using Mayer cluster expansion with a new generating function. The thermodynamic properties and equation of state of non ideal system has got great importance at high densities, where the system will show the phase transition [1, 2, 3, 4, 5].

The van der Waals model [8] was the first known example of an interacting system derived phenomenologically. This model explains the existence of molecular structure, interactions between particles and provided an explanation for phase transition, which can be derived by using mean field methods [5] or by using cluster expansion [1,2,3,4]. In mean field approximation an interacting system is approximated by a non interacting system in a self-consistent external field. In another way an approximate free energy is expressed in terms of an unknown parameter, and the free energy is then minimized with respect to that parameter to study the phase transition. Mean field method is applicable to interacting many particle systems such as fluids, magnets, binary alloys etc. [5, 9] to study the thermodynamic properties and phase transition. For non polar molecules the mutual interaction potential like Lennard- Jones, normally arises due to the orbital charge cloud fluctuations and due to the hard core repulsion of the molecules. When the particles possess permanent dipole moments of electric or magnetic nature as in polar gases, then the dipole-dipole interactions will be the dominating factor which effects the thermodynamic properties of the system and such a system can be treated as an interacting system. The long range and anisotropic character of dipole dipole interactions makes dipolar systems unique. These forces can be partially repulsive and partially attractive and this makes the dipole dipole interaction have very important consequences for the scattering properties of the particles in ultra-cold gas [10]. The increased level of experimental control, together with specific physical properties of dipole-dipole interactions, provide a unique possibility to find new physical phenomena and practical applications [10]. These unique properties of dipolar systems are utilised   in the production of Bose Einstein Condensate of polar molecules at low temperatures [10].

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Potential energy for a dipolar system

Consider a system of identical molecules on a lattice with permanent electric dipole moment in the absence of any external field. The electric field due to the first dipole at a distance r_{12} is given by

$$\vec{E}_1 = \frac{1}{4\pi\varepsilon_0} \frac{3(\hat{r}_{12}.\vec{p}_1)\hat{r}_{12}-\vec{p}_1}{r_{12}^3} \tag{1}$$

In the presence of another dipole at a distance r_{12} with dipole moment $\vec{p}_2$, the interaction energy is given by $U_{12} = -\vec{p}_2.\vec{E}_1$

$$U_{12} = \frac{-1}{4\pi\varepsilon_0} \frac{3(\hat{r}_{12}.\vec{p}_1)(\hat{r}_{12}.\vec{p}_2)-\vec{p}_1.\vec{p}_2}{r_{12}^3} \tag{2}$$

The potential energy of the molecule 1 with all other molecules in the system (ε_1) can be calculated using the mean field approximation by taking average over the orientations of jth dipole molecule with dipole moment $\vec{p}_j$, this is taken as average dipolemoment $\langle\vec{p}\rangle$ [9], then

$$\varepsilon_1 = -\vec{p}_1.\sum_j \left(\frac{3(\hat{r}_{1j}.\langle\vec{p}\rangle)\hat{r}_{1j}-\langle\vec{p}\rangle}{4\pi\varepsilon_0 r_{1j}^3} \right) \tag{3}$$

This equation can be written as

$$\varepsilon_1 = -\vec{p}_1.\vec{E}_l \tag{4}$$

where $\vec{E}_l$ is the local field given by

$$\vec{E}_l = \sum_j \left(\frac{3(\hat{r}_{1j}.\langle\vec{p}\rangle)\hat{r}_{1j}-\langle\vec{p}\rangle}{4\pi\varepsilon_0 r_{1j}^3} \right) = \frac{a}{4\pi\varepsilon_0} \vec{P}_e \tag{5}$$

where a is a dimensionless term coming from the sample shape, $\vec{P}_e = \rho\langle\vec{p}\rangle$ is the polarization, and $\rho = \frac{N}{V}$ is the number density of particles in the system. Since all the dipoles are of equal dipolemoment p

$$\varepsilon_1 = -\vec{p}_1.\vec{E}_l = -c\rho p P_e cos\theta \tag{6}$$

where $c = \frac{a}{4\pi\varepsilon_0\rho} = \frac{\alpha}{\rho}$ with $\alpha = \frac{a}{4\pi\varepsilon_0}$ and θ is the angle between $\vec{p}_1$ and $\vec{P}_e$. This single particle potential correctly predict the torque acting on the molecule 1 due to all other molecules, but this value over counts the mean value by a factor of 2. Then the suitable single particle potential can be obtained as [9]

$$u_1 = \varepsilon_1 - \frac{1}{2}\langle\varepsilon_1\rangle \tag{7}$$

In this case it can be shown that[9]

$$u_1 = -c\rho p P_e cos\theta + \frac{1}{2}c P_e^2 \tag{8}$$

This equation gives the correct average energy $U = N\langle u_1\rangle$ with out taking the criteria of over counting of pair potential. Then total interaction energy of the system is

$$U = -Nc\rho p P_e cos\theta + \frac{1}{2}Nc P_e^2$$

$$(9)$$

So the total energy is

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + -Nc\rho p P_e cos\theta + \frac{1}{2}NcP_e^2 \tag{10}$$

Calculation of Number of micro states

The hard core nature of interacting dipoles prevents two dipoles come closer than the diameter of the dipole molecule ($d = 2\sigma$). If the system contains N particles, the difference between actual physical volume (V) and the excluded volume for dipoles gives the corrected volume (V') .

$$V' = V - Nb' \tag{11}$$

where $b' = \frac{2\pi d^3}{3}$.

The total number of micro states (Ω) is given by [1, 2, 3, 4, 5]

$$\Omega = \frac{Total phase space volume}{N! h^{3N}} \tag{12}$$

$$\Omega = \frac{(V-Nb')^N V_p}{N! h^{3N}} \tag{13}$$

where   is the spatial volume available for N particles, $N!$ is used as the Gibbs correction term, and V_p is the volume of 3N dimensional momentum sphere.

$$V_p = \frac{\pi^{\frac{3N}{2}} R^{3N}}{\left(\frac{3N}{2}\right)!} \tag{14}$$

Using the equation for total energy of dipolar system, the radius of hyper sphere is

$$R = \sqrt{2m\left[E - \left(-Nc\rho p P_e cos\theta + \frac{1}{2}NcP_e^2\right)\right]} \tag{15}$$

Then the total number of micro states can be calculated as

$$\Omega = \tag{16}$$

By Boltzmann's equation, statistical entropy S is given by

$$S = kln\Omega \tag{17}$$

Substituting Ω

$$S = \frac{5}{2}Nk + Nkln\left(\frac{V-Nb'}{N}\right) + Nkln\left[\left(\frac{4\pi m}{3Nh^2}\right)\left(E + Nc\rho p P_e cos\theta - \frac{1}{2}NcP_e^2\right)\right]^{\frac{3}{2}} \tag{18}$$

Knowing the value of entropy and using the first law of thermodynamics, the thermodynamic properties can be calculated. We have,

$$TdS = dE + PdV - \mu dN \tag{19}$$

where T is the absolute temperature, P is the pressure and μ is the chemical potential.

The equation of state can be obtained from

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} \tag{20}$$

$$\frac{P}{T} = \frac{Nk}{V - Nb'} - \frac{3}{2}Nk\left[\frac{\alpha P_e^2}{2}\frac{1}{\left(E - \frac{1}{2}NcP_e^2 + Nc\rho p P_e \cos\theta\right)}\right] \tag{21}$$

The value of E can be calculated from

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \tag{22}$$

$$E = \frac{3}{2}NkT + \left(\frac{1}{2}NcP_e^2 - Nc\rho p P_e \cos\theta\right) \tag{23}$$

Substituting the value of E, the equation of state is obtained from Eq.(21) as

$$\left(P + \frac{\alpha P_e^2}{2}\right)(V - Nb') = NkT \tag{24}$$

If total polarization is represented interms of number density of particles, this non ideal equation of state takes the form similar to the van der Waals equation of state.

Conclusions

Finding the equation of state and thermodynamics of a real physical system is an important area in statistical mechanics. Here we discussed a system of dipolar particles with permanent electric dipole-dipole interaction, and make use of the mean field theory to derive the non ideal equation of state and thermodynamics. The equation of state takes the form of the van der Waals equation when the polarization is taken as a function of number density.

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