

Thermodynamic Properties of the Ionized Gas ${}^3\text{He}$

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Thermodynamic properties of singly ionized gas ${}^3\text{He}$ at finite temperatures have been investigated using the second quantization method. Calculations have been done for a quasi-neutral system in the temperature range 30000-40000 K. We have used the first order perturbation method to calculate the interaction energy. The free energy, specific heat and pressure have been computed.

Keywords: Ionized gas ${}^3\text{He}$, Second quantization method

INTRODUCTION

At the present time the importance of study of various properties of ionized gases has considerably increased. Because of their sizable temperature and density range, ionized gases find applications in many fields of research, technology and industry. The quantum statistical mechanics of dense ionized gases has been studied intensively [1-3] and numerous theoretical developments have appeared which can significantly improve the calculation of thermodynamic equilibrium compositions and properties of strongly ionized gases. Thermodynamic properties of fully or partial ionized gases have been investigated by application of several methods and considering different conditions [4-10].

Helium is of special interest physical system from both experimental and theoretical points of view. Helium atom as the simplest many-electron system and one of the lightest elements, provides a lucid way for testing the quantum statistical theories of matter. Thermodynamic treatment of helium makes it to be exploited in a number of high-technology applications. Prior calculations of the thermodynamic properties of helium have been carried out by several investigators using a variety of models [11-16].

Helium gas, as the most inert among the inert gases has the highest ionization potential (24.587 eV) and the lowest

polarizability (0.205 \AA^{-3}) [17] of all chemical elements. The interest in ${}^3\text{He}^+$ is strongly related to the "hot" topic of helium clusters and super fluid helium droplets. ${}^3\text{He}^+$ was first observed in 1968 by Patterson [18]. It has been the subject of numerous theoretical studies [19-37]. Very recently, Eisazadeh-Far *et al.* [38] have calculated the thermodynamic properties at high temperatures using statistical mechanical methods over the temperature range 300-100000 K.

In this paper we carry out a detailed study of the thermodynamic properties of ionized gas ${}^3\text{He}$ using the second quantization method. The formalism of method reformulates the schrödinger equation of system in a way that greatly facilitates solving it for an interacting many-body system, directly. Our calculations is made over the temperature range 30000-40000 K. Here we calculate some properties of system such as the free energy, heat capacity and pressure. In the next two sections, we describe the details of the second quantization method for computing the internal energy of dense ionized gas ${}^3\text{He}$. The section 3 is concerned with the obtained results and corresponding discussions. Summarizing conclusions are expressed in the last section.

THE SECOND QUANTIZATION METHOD

To study the energy of ionized gas ${}^3\text{He}$, we consider a quasi-neutral system, containing electrons and ions with

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equal number density ($\rho = \frac{N}{V}$). Here, the sum of kinetic and potential energies of the electrons system and the ions system are treated independently, and an independent term is also considered due to the interaction between these two systems. The Hamiltonian of the system is written as follows:

$$\mathbf{H} = \mathbf{H}_{el} + \mathbf{H}_{ion} + \mathbf{H}_{el-ion}, \quad (1)$$

where \mathbf{H}_{el} and \mathbf{H}_{ion} are single-particle kinetic operator and two-body interaction operator for electrons and ions, respectively. \mathbf{H}_{el-ion} denotes interaction operator between electrons and ions. Assuming the interaction between charged particles to be of Debye form $\frac{ze^2 e^{-\mu r_{ij}}}{r_{ij}}$, in which μ is the screening length parameter, the Hamiltonian becomes:

$$\begin{aligned} H_{el} &= \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu r_{ij}}}{r_{ij}} \\ H_{ion} &= \sum_{i=1}^N \frac{P_i^2}{2M} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu R_{ij}}}{R_{ij}} \\ H_{el-ion} &= -e^2 \sum_{i=1}^N \sum_{j=1}^N \frac{e^{-\mu|r_i - R_j|}}{|r_i - R_j|}, \end{aligned} \quad (2)$$

where m and M are masses of electron and ion, respectively. The second quantization method involves using the so-called creation and annihilation operators, which create and annihilate particles in a specified single-particle state. It can be seen that the anti-symmetry property of fermions manifests itself in characteristic anti-commutation relations obeyed by these operators. In term of creation and annihilation operators, the expression for the one-body and two-body operators in the second quantization formalism are given by [39],

$$\begin{aligned} \hat{o}_1 &= \sum_{i=1}^N \hat{o}_1(x_i) = \sum_{\lambda, \lambda'} b_{\lambda}^{\dagger} \langle \lambda | b_1(x_i) | \lambda' \rangle b_{\lambda'} \\ \hat{o}_2 &= \frac{1}{2} \sum_{i,j} \hat{o}_2(x_i, x_j) = \sum_{\lambda, \lambda', \mu, \mu'} b_{\lambda}^{\dagger} b_{\mu}^{\dagger} \langle \lambda, \mu | b_2(x_i, x_j) | \lambda', \mu' \rangle b_{\lambda'} b_{\mu'} \end{aligned} \quad (3)$$

The advantage of this representation is that it can be applied

for both bosons and fermions. Using Eq. (3), the individual terms of the Hamiltonian (Eq. (2)) are easily rewritten in the second quantization formalism,

$$\begin{aligned} H_{el} &= \frac{1}{2m} \sum_{\substack{k, k' \\ \lambda, \lambda'}} a_{k\lambda}^{\dagger} \langle k\lambda | p^2 | k'\lambda' \rangle a_{k'\lambda'} \\ &+ \frac{e^2}{2V} \sum_{\substack{k_1, k_2, k_3, k_4 \\ \lambda_1, \lambda_2, \lambda_3, \lambda_4}} a_{k_1 \lambda_1}^{\dagger} a_{k_2 \lambda_2}^{\dagger} \langle k_1 \lambda_1, k_2 \lambda_2 | \frac{e^{-\mu r_{ij}}}{r_{ij}} | k_3 \lambda_3, k_4 \lambda_4 \rangle a_{k_4 \lambda_4} a_{k_3 \lambda_3} \\ H_{ion} &= \frac{1}{2M} \sum_{\substack{K, K' \\ \xi, \xi'}} a_{K\xi}^{\dagger} \langle K\xi | P^2 | K'\xi' \rangle a_{K'\xi'} \\ &+ \frac{e^2}{2V} \sum_{\substack{K_1, K_2, K_3, K_4 \\ \xi_1, \xi_2, \xi_3, \xi_4}} a_{K_1 \xi_1}^{\dagger} a_{K_2 \xi_2}^{\dagger} \langle K_1 \xi_1, K_2 \xi_2 | \frac{e^{-\mu R_{ij}}}{R_{ij}} | K_3 \xi_3, K_4 \xi_4 \rangle a_{K_4 \xi_4} a_{K_3 \xi_3} \\ H_{el-ion} &= \frac{-e^2}{V} \sum_{\substack{k_1, k_2, K_1, K_2 \\ \lambda_1, \lambda_2, \xi_1, \xi_2}} a_{k_1 \lambda_1}^{\dagger} a_{k_2 \lambda_2}^{\dagger} \langle k_1 \lambda_1, K_1 \xi_1 | \frac{e^{-\mu|r_i - R_j|}}{r_i} - R_j | k_2 \lambda_2, K_2 \xi_2 \rangle a_{K_2 \xi_2} a_{k_2 \lambda_2}, \end{aligned}$$

where k and K are the wave vectors of electrons and ions respectively.

In order to calculate \mathbf{H}_{el} , it is needed to get the matrix elements given in Eq. (4). Since the periodic boundary conditions give the current carrying eigenstates being well suited for the description of transport phenomena, the following single particle wave function is considered as the single-particle basis states,

$$\Psi = \frac{1}{\sqrt{V}} e^{-ik \cdot r} \eta_{\lambda} = \langle r | k \lambda \rangle \quad (7)$$

Here, using the above single particle wave function, the mentioned matrix elements can be computed,

$$\begin{aligned} \langle k \lambda | p^2 | k' \lambda' \rangle &= \int dr \frac{1}{\sqrt{V}} e^{-ik_1 \cdot r} \eta_{\lambda_1}^{\dagger} (-\hbar^2 \nabla^2) \frac{1}{\sqrt{V}} e^{ik_2 \cdot r} \eta_{\lambda_2} \\ &= \hbar^2 k_2^2 \delta_{k_1, k_2} \end{aligned} \quad (8)$$

Substituting Eqs. (8) and (9) in Eq. (4) leads to the

$$\begin{aligned} \langle k_1 \lambda_1, k_2 \lambda_2 \left| \frac{e^{-\mu r_{ij}}}{r_{ij}} \right| k_3 \lambda_3, k_4 \lambda_4 \rangle &= \frac{e^2}{V^2} \int dr_2 \int dr_1 e^{-ik_1 \cdot r_1} \eta_{\lambda_1}^\dagger e^{-ik_2 \cdot r_2} \eta_{\lambda_2}^\dagger \frac{e^{-\mu|r_1-r_2|}}{|r_1-r_2|} e^{ik_3 \cdot r_1} \eta_{\lambda_3}^\dagger e^{ik_4 \cdot r_1} \eta_{\lambda_4}^\dagger \\ &= \frac{e^2}{V} \delta_{mbda_1, \lambda_3} \delta_{\lambda_2, \lambda_4} \delta_{k_1+k_2, k_3+k_4} \frac{4\pi}{|k_4 - k_2|^2 + \mu^2} \end{aligned} \quad (9)$$

following relation for H_{el} ,

$$H_{el} = \sum_{k, \lambda} \frac{\hbar^2 k^2}{2m} \hat{n}_{k\lambda} + \frac{1}{2V} \sum_q \sum_{k_1, k_3} \sum_{\lambda, \lambda'} \frac{4\pi e^2}{q^2} + \mu^2 \hat{n}_{k_3+q, bda} \hat{n}_{k_3, \lambda'} \quad (10)$$

where $\vec{q} = \vec{k}_1 - \vec{k}_3$. In above equation, $\hat{n}_\alpha = a_\alpha^\dagger a_\alpha$ is called number operator. In order to find the expectation value of H_{el} , we consider it as two different parts, $\langle H_{el} \rangle = E_{kin} + E_{pot}$ which are related to the kinetic and potential energies, respectively. The kinetic energy E_{kin} and potential energy E_{pot} are as follows,

$$E_{kin} = \sum_{k, \lambda} \frac{\hbar^2 k^2}{2m} \langle FS | \hat{n}_{k\lambda} | FS \rangle, \quad (11)$$

$$E_{pot} = \frac{1}{2V} \sum_{q \neq 0} \sum_{k_1, k_3} \sum_{\lambda, \lambda'} \frac{4\pi e^2}{q^2} \langle FS | \hat{n}_{k_3+q, \lambda} \hat{n}_{k_3, \lambda'} | FS \rangle. \quad (12)$$

Clearly, the ground state for N electrons in occupation number representation, $|FS\rangle$, is obtained by filling up the N states with the lowest possible energy. Note that the density dependence of kinetic energy, $E_{kin} \propto \rho^{\frac{5}{3}} \exp(-\rho^{\frac{2}{3}})$, in comparison with that of potential energy, $E_{pot} \approx (\frac{e^2}{d}) \propto \exp(-\rho^{\frac{2}{3}})$, shows that the system actually serves as a starting point for a perturbation expansion. Here, the first order calculation is being considered in the thermodynamic limit such that the number density (ρ) stays fixed. Here, we note that the procedure of calculation of the expectation values of H_{ion} and H_{el-ion} is the same as done for that of H_{el} .

Now by calculating the total energy of the system (E), and considering the entropy of system by

$$S = -k_B \sum_k [n(k) \ln n(k) + (1-n(k)) \ln(1-n(k))], \quad (13)$$

Where $n(k)$ is Fermi-Dirac distribution function [39], the free energy of the system can be determined as follows

$$A = E - TS. \quad (14)$$

Finally, the thermodynamic properties of ionized gas ³He can be obtained.

RESULTS AND DISCUSSION

To study the thermodynamics of ionized gas ³He in more details, several thermodynamic properties have been calculated. We performed second quantization formalism for number density (ρ) ranging from 4×10^{21} to 1.4×10^{22} cm⁻³ at different values of temperature, *i.e.* $T = 30000-40000$ K. We start by presenting our results for the free energy per particle of the gas versus density presented in Fig. 1. As one expects by increasing the density (temperature), the free energy increases (decreases). According to the second law of thermodynamics, the entropy of system is always positive. By increasing the temperature, the magnitude of second term in Eq. (14) rises and, therefore, the free energy of system decreases. It can be seen that, the free energy shows no minimum (saturation point). We readily observe that at high densities the curves of different temperatures merge to each other which implies the trivial influence of temperature on free energy as well as the internal energy at this region. The figure shows that the free energy at $T = 0$ K varies more slowly than that at finite temperatures.

The specific heat of the gas can be obtained by differentiating internal energy with respect to T , keeping N and V constant. Figure 2 shows the specific heat versus temperature for two different values of density. It is seen

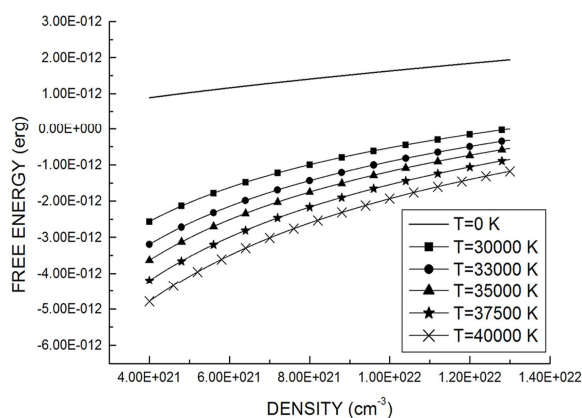


Fig. 1. The free energy per particle vs. density for different values of temperature (T).

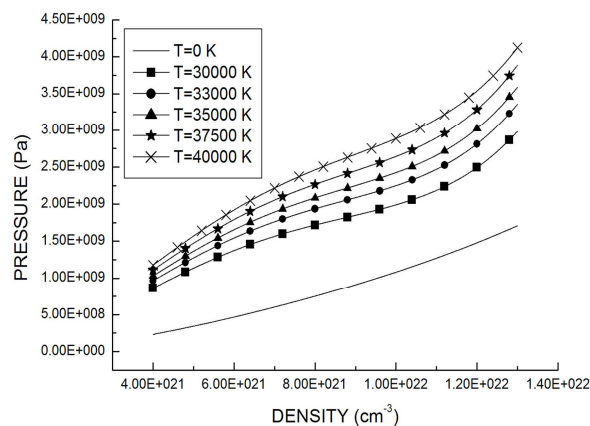


Fig. 3. The pressure vs. density for different values of temperature (T).

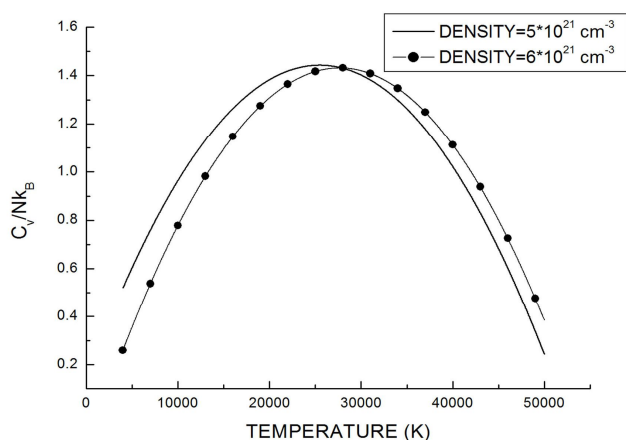


Fig. 2. The specific heat vs. temperature for different values of density.

that the specific heat increases monotonically with temperature until a specific temperature, then it decreases by increasing the temperature, and finally falls to zero. The result is the appearance of a maximum in the specific heat of system. The peak is an indication of chemical reactions in the ionized gas [40]. We also see that by increasing the density, the maximum value of specific heat happens at higher temperature. The magnitude of specific heat at maximum point decreases by increasing density. Extrapolating the data in Fig. 2 indicates that C_V appears to be approaching zero as $T \rightarrow 0$. Therefore, It can be

concluded that all degrees of freedom are frozen. In other word, the vanishing reflects the fact that there are no available states in which to deposit energy at low temperature, since almost all states below Fermi energy are occupied.

The pressure of system versus density (equation of state) has been plotted in Fig. 3. It is seen that for all temperatures, pressure increases monotonically by increasing the density and temperature, however, the degree of sloping at which the pressure increases is also noteworthy. This figure shows that at low densities, the pressure increases linearly as the density increases. As ρ increases, the increase of pressure becomes smoother for the region $6.2 \times 10^{21} \text{ cm}^{-3} < 1.04 \times 10^{22} \text{ cm}^{-3}$. For densities greater than about $1.04 \times 10^{22} \text{ cm}^{-3}$ the pressure behaves stiffer. Incidentally, at low densities, the difference between the pressure of different temperatures decreases. Figure 3 also shows that the equation of state of ionized gas ^3He becomes stiffer as the temperature increases. Our results show that the pressure is proportional to temperature, but the relation is not linear as classical ideal gas.

SUMMARY AND CONCLUSIONS

In this article, we have calculated some thermodynamic properties for a system consisting of singly ionized ^3He atoms and their corresponding removed electrons by employing the second quantization method at finite

temperature. To perform the calculations, we have considered the kinetic term, and Coulomb interaction between the particles in our Hamiltonian. The calculated properties are free energy, specific heat and pressure. It is shown that all these quantities are very temperature sensitive. For all temperatures and densities, we have seen that the main contribution to the internal energy comes from the kinetic term.

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