PHYSICAL REVIEW A VOLUME 30, NUMBER 2 AUGUST 1984

Equilibrium properties of molecular fluids in the semiclassical limit

A. K. Singh* and S. K. Sinha
Department of Physics, Langat Singh College, Bihar University, Muzaffarpur 842001, Bihar, India

(Received 13 December 1983)

The quantum corrections to the thermodynamic properties of simple molecular fluids have been calculated, with the influence of quadrupole moment, induced dipole moment, anisotropic dispersion, and shape factors taken into account. Expressions are given for the free energy, pressure, entropy, and internal energy, and results are reported for D_2 and H_2. It may be seen that the rotational contribution to the quantum effect is very small in comparison to the translational contribution, in which the main contribution arises from the central forces.

I. INTRODUCTION

The problem of calculating the structural and thermodynamic properties of molecular fluids made of nonspherical molecules has been a subject of considerable interest in recent years.[1] Although the behavior of fluids is fundamentally quantum mechanical, most of the fluids found in the literature have been treated classically because the quantum effects for them are so small as to be negligible.[2]

There are some fluids, such as H_2 and D_2, for which deviations from classical behavior are observed at low temperatures. For classical molecular fluids considerable progress has been made.[3-15] However, our understanding of the quantum molecular fluids is far from satisfactory.[16]

In the semiclassical limit (i.e., high-temperature limit), where quantum effects are small and can be treated as a correction to the classical system, the usual method for calculating such quantum corrections is the Wigner-Kirkwood (WK) expansion.[17,18] In this approach, expansion is done in powers of the kinetic energy operator $\hbar^2\nabla^2$, which leads to a series in powers of $\hbar^2$. Since ∇^2 operates on the potential-energy term, the WK-expansion method is valid for analytic potentials. This method has been used extensively to calculate the equilibrium properties of fluids of spherical molecules.[19]

The WK method can be extended to cases where the intermolecular potential is a complicated function of both positions and orientations of the molecules.[20] For such a fluid, the only work available is that of Wang Chang[16,21] and Singh and Datta,[22] who have calculated the quantum corrections to the second virial coefficient of diatomic fluids. Singh and Datta[22] have considered the various factors which arise due to the presence of permanent and induced electric moments and the shape of the molecules. For diatomic molecules, which may be represented by rigid three-dimensional rotators of mass m and moment of inertia I, the quantum corrections are the sum of two parts: one is due to the translational contributions and the other is due to the rotational contributions. To the best of our knowledge, no work is available for the dense molecular fluids in the semiclassical limit.

The present paper is concerned with the evaluation of the equilibrium properties of the dense molecular fluids in the semiclassical limit. We assume that the total interaction potential is pairwise additive, i.e.,

$$U(\overline{X}_1,\overline{X}_2,\ldots,\overline{X}_N)=\sum_{1\le i<j\le N} u(\overline{X}_i,\overline{X}_j)\ , \tag{1.1}$$

where $u(\overline{X}_i,\overline{X}_j)$ is the pair potential between molecules i and j and the vector $\overline{X}_i\equiv(\overline{r}_i,\omega_i)$ represents both the position of the center of mass and orientation of the ith molecule. The pair interaction potential between two diatomic molecules is usually assumed to be of the form

$$u(\overline{X}_i,\overline{X}_j)=u_0(\overline{r}_i,\overline{r}_j)+u_a(\overline{X}_i,\overline{X}_j)\ , \tag{1.2}$$

where $u_0(\overline{r}_i,\overline{r}_j)$ is a spherically symmetric component and $u_a(\overline{X}_i,\overline{X}_j)$ a contribution due to the nonsphericity of the molecular charge distribution. The anisotropic contribution $u_a(\overline{X}_i,\overline{X}_j)$ in Eq. (1.2) is conveniently divided into the classical electrostatic interaction, the anisotropy of the quantum-mechanical dispersion forces, and the anisotropy of the repulsive part of interaction potential (i.e., shape of the molecular core). In the present treatment we neglect the three-body nonadditive interaction.

In Sec. II we give the basic theory for calculating the radial distribution function (RDF) and thermodynamic properties of molecular fluids in the semiclassical limit. Expressions are given there for the free energy and RDF in terms of the classical distribution functions. Section III is devoted to discussing the perturbation theory in which nonspherical potentials are treated as perturbation for the thermodynamic properties and RDF of classical molecular fluids. In Sec. IV the first-order quantum correction to the thermodynamic properties is simplified and expressed in terms of the distribution functions of classical fluid whose molecules interact via the central potential. Results are discussed in Sec. V. The concluding remarks are given in Sec. VI.

II. BASIC THEORY

A. Expansion of Slater sum

We consider molecular fluids of diatomic molecules which are permanently in their ground electronic and ground vibrational states. Thus the diatomic molecules may be represented by rigid three-dimensional rotators of mass m and moment of inertia I, each with five degrees of freedom—three translational and two rotational.

The quantity of central importance for constructing the theory of semiclassical fluid is the Slater sum, which may be defined in this case as

$$W_N(\bar{X}_1,\bar{X}_2,\ldots,\bar{X}_N)=N!\lambda_{\rm tr}^{3N}\lambda_{\rm rot}^{2N}\sum_{\chi}\psi_\chi^*\exp(-\beta\hat{H}_N)\psi_\chi\ , \tag{2.1}$$

where

$$\lambda_{\rm tr}=(2\pi\hbar^2\beta/m)^{1/2}\ , \tag{2.2a}$$

$$\lambda_{\rm rot}=(2\pi\hbar^2\beta/I)^{1/2}\ , \tag{2.2b}$$

and $\beta=(kT)^{-1}$. Here ψ_χ's are a complete set of orthogonal N-particle wave functions. The summation in Eq. (2.1) extends over all states. $\hat{H}_N$ is the Hamiltonian of the system

$$\hat{H}_N=-\frac{\hbar^2}{2m}\sum_i\nabla_i^2+U\ , \tag{2.3}$$

where ∇_i^2 is the generalized Laplacian operator in an s-dimensional space. In this case ∇_i^2 is given by

$$-\frac{\hbar^2}{2m}\nabla_i^2=-\frac{\hbar^2}{2m}\nabla_{r_i}^2-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta_i}\frac{\partial}{\partial\theta_i}\left[\sin\theta_i\frac{\partial}{\partial\theta_i}\right]+\frac{1}{\sin^2\theta_i}\frac{\partial^2}{\partial\varphi_i^2}\right]\ . \tag{2.4}$$

In the semiclassical limit, where the quantum effects are small, we follow the method of Friedmann[20] and write the expansion of W_N as

$$\begin{aligned}W_N(\bar{X}_1,\bar{X}_2,\ldots,\bar{X}_N)=\exp(-\beta U)\Bigg[1-\Bigg\{\left[\frac{\hbar^2\beta}{12m}\right]^2\sum_{i=1}^{N}[\nabla_{r_i}^2U-\tfrac{1}{2}\beta(\vec{\nabla}_{r_i}U)^2]\\+\left[\frac{\hbar^2\beta}{12I}\right]^2\sum_{i=1}^{N}\left[\frac{1}{\sin\theta_i}\frac{\partial}{\partial\theta_i}\left[\sin\theta_i\frac{\partial U}{\partial\theta_i}\right]+\frac{1}{\sin^2\theta_i}\frac{\partial^2U}{\partial\varphi_i^2}-\frac{\beta}{2}\left[\frac{\partial U}{\partial\theta_i}\right]^2\right.\\\left.-\frac{\beta}{2}\frac{1}{\sin^2\theta_i}\left[\frac{\partial U}{\partial\varphi_i}\right]^2\right]\Bigg\}+O(\hbar^4)\Bigg]\ .\end{aligned} \tag{2.5}$$

Using Eq. (1.1), Eq. (2.5) can be written as

$$\begin{aligned}W_N(\bar{X}_1,\bar{X}_2,\ldots,\bar{X}_N)=\exp\left[-\beta\sum_{\substack{i,j=1\\i<j}}^{N}u(\bar{X}_i,\bar{X}_j)\right]\\\times\left[1+\sum_{\substack{i,j=1\\i<j}}^{N}U_2^m(\bar{X}_i,\bar{X}_j)+\sum_{\substack{i,j,k=1\\i<j<k}}^{N}U_3^m(\bar{X}_i,\bar{X}_j,\bar{X}_k)+\sum_{\substack{i,j,k,l=1\\i<j\neq k<l}}^{N}U_2^m(\bar{X}_i,\bar{X}_j)U_2^m(\bar{X}_k,\bar{X}_l)+\cdots\right]\ ,\end{aligned} \tag{2.6}$$

where

$$U_2^m(\bar{X}_i,\bar{X}_j)=\left[\frac{\hbar^2\beta}{m}\right]U_2^{\rm tr}(\bar{X}_i,\bar{X}_j)+\left[\frac{h^2\beta}{I}\right]U_2^{\rm rot}(\bar{X}_i,\bar{X}_j)\ , \tag{2.7}$$

$$U_3^m(\bar{X}_i,\bar{X}_j,\bar{X}_k)=\left[\frac{\hbar^2\beta}{m}\right]U_3^{\rm tr}(\bar{X}_i,\bar{X}_j,\bar{X}_k)+\left[\frac{\hbar^2\beta}{I}\right]U_3^{\rm rot}(\bar{X}_i,\bar{X}_j,\bar{X}_k)\ . \tag{2.8}$$

Here $U_l^{\rm tr}$ and $U_l^{\rm rot}$ are the l-particle "modified" Ursell functions due to translational and rotational contributions, respectively, and are given by

$$U_2^{\rm tr}(\bar{X}_i,\bar{X}_j)=-\frac{\beta}{6}\{\nabla_{r_{ij}}^2u(\bar{X}_i,\bar{X}_j)-\tfrac{1}{2}\beta[\vec{\nabla}_{r_{ij}}u(\bar{X},\bar{X}_j)]^2\}\ , \tag{2.9a}$$

$$\begin{aligned}U_3^{\rm tr}(\bar{X}_i,\bar{X}_j,\bar{X}_k)=\frac{\beta^2}{12}[\vec{\nabla}_{r_i}u(\bar{X}_i,\bar{X}_j)\cdot\vec{\nabla}_{r_i}u(\bar{X}_i,\bar{X}_k)\\+\vec{\nabla}_{r_j}u(\bar{X}_i,\bar{X}_j)\cdot\vec{\nabla}_{r_j}u(\bar{X}_j,\bar{X}_k)\\+\vec{\nabla}_{r_k}u(\bar{X}_i,\bar{X}_k)\cdot\vec{\nabla}_{r_k}u(\bar{X}_j,\bar{X}_k)]\end{aligned} \tag{2.9b}$$

and

$$
\begin{aligned}
U_2^{\mathrm{rot}}(\bar{X}_i,\bar{X}_j) = -\frac{\beta}{12}\Bigg[& \frac{1}{\sin\theta_i}\frac{\partial}{\partial\theta_i}\left[\sin\theta_i\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\theta_i}\right]+\frac{1}{\sin\theta_j}\frac{\partial}{\partial\theta_j}\left[\sin\theta_j\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\theta_j}\right] \\
& +\frac{1}{\sin^2\theta_i}\frac{\partial^2 u(\bar{X}_i,\bar{X}_j)}{\partial\phi_i^2}+\frac{1}{\sin^2\theta_j}\frac{\partial^2 u(\bar{X}_i,\bar{X}_j)}{\partial\varphi_j^2}-\frac{\beta}{2}\left[\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\theta_i}\right]^2-\frac{\beta}{2}\left[\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\theta_j}\right]^2 \\
& -\frac{\beta}{2}\frac{1}{\sin^2\theta_i}\left[\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\phi_i}\right]^2-\frac{\beta}{2}\frac{1}{\sin^2\theta_j}\left[\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\varphi_j}\right]^2\Bigg] ,
\end{aligned}
\tag{2.10a}
$$

$$
\begin{aligned}
U_3^{\mathrm{rot}}(\bar{X}_i,\bar{X}_j,\bar{X}_k) = \frac{\beta^2}{24}\Bigg\{ & \Bigg[\left[\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\theta_i}\right]\left[\frac{\partial u(\bar{X}_i,\bar{X}_k)}{\partial\theta_i}\right]+\left[\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\theta_j}\right]\left[\frac{\partial u(\bar{X}_j,\bar{X}_k)}{\partial\theta_j}\right]+\left[\frac{\partial u(\bar{X}_i,\bar{X}_k)}{\partial\theta_k}\right]\left[\frac{\partial u(\bar{X}_j,\bar{X}_k)}{\partial\theta_k}\right]\Bigg] \\
& +\Bigg[\frac{1}{\sin^2\theta_i}\left[\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\varphi_i}\right]\left[\frac{\partial u(\bar{X}_i,\bar{X}_k)}{\partial\varphi_i}\right]+\frac{1}{\sin^2\theta_j}\left[\frac{\partial u(\bar{X}_i,\bar{X}_j)}{\partial\varphi_j}\right]\left[\frac{\partial u(\bar{X}_j,\bar{X}_k)}{\partial\varphi_j}\right] \\
& +\frac{1}{\sin^2\theta_k}\left[\frac{\partial u(\bar{X}_i,\bar{X}_k)}{\partial\varphi_k}\right]\left[\frac{\partial u(\bar{X}_j,\bar{X}_k)}{\partial\varphi_k}\right]\Bigg]\Bigg\} .
\end{aligned}
\tag{2.10b}
$$

Thus the contribution of the first order of $\hbar^2$, which arises due to the translational and rotational contributions, comes from both U_2^m and U_3^m.

B. Free energy

The quantum-mechanical canonical partition function for a molecular fluid is defined as

$$
Q_N=(N!\lambda_{\mathrm{tr}}^{3N}\lambda_{\mathrm{rot}}^{2N}\Omega^N)^{-1} \times\int\cdots\int W_N(\bar{X}_i,\ldots,\bar{X}_N)\prod_{i=1}^{N}d\bar{X}_i , \tag{2.11}
$$

where

$$
d\bar{X}_i\equiv d\bar{r}_i\,d\omega_i=d\bar{r}_i\,\sin\theta_i\,d\theta_i\,d\varphi_i \tag{2.12}
$$

and $\Omega=4\pi$ for linear molecules. Once the partition function is known, the thermodynamic properties can be obtained. Thus the free energy of the system is given by

$$
A=-kT\ln Q_N . \tag{2.13}
$$

Substituting Eq. (2.5) into Eq. (2.11) and integrating by parts, we obtain an expression for the free energy correct to the first order of $\hbar^2$:

$$
\frac{\beta A}{N}=\frac{\beta A^c}{N}+\left[\frac{\hbar^2\beta}{m}\right]\left[\frac{A_{\mathrm{tr}}^I}{N}\right]+\left[\frac{\hbar^2\beta}{I}\right]\left[\frac{A_{\mathrm{rot}}^I}{N}\right]+O(\hbar^4) , \tag{2.14}
$$

where

$$
\left[\frac{A_{\mathrm{tr}}^I}{N}\right]=\frac{\rho\beta}{192\pi}\int g^c(\bar{X}_1,\bar{X}_2)\nabla_r^2 u(\bar{X}_1,\bar{X}_2)\,d\bar{r}\,d\omega , \tag{2.15}
$$

$$
\left[\frac{A_{\mathrm{rot}}^I}{N}\right]=\frac{\rho\beta}{192\pi}\int g^c(\bar{X}_1,\bar{X}_2)\left[\frac{1}{\sin\theta_1}\frac{\partial}{\partial\theta_1}\left[\sin\theta_1\frac{\partial u(\bar{X}_1,\bar{X}_2)}{\partial\theta_1}\right]+\frac{1}{\sin^2\theta_i}\frac{\partial^2 u(\bar{X}_1,\bar{X}_2)}{\partial\varphi_1^2}\right]d\bar{r}\,d\omega , \tag{2.16}
$$

with

$$
d\omega=\sin\theta_1\,d\theta_1\sin\theta_2\,d\theta_2\,d\varphi ,
$$

where A^c and $g^c(\bar{X}_1,\bar{X}_2)$ are, respectively, the free energy and RDF for the classical molecular fluid. Other thermodynamical properties can be obtained from the free energy.

C. Radial distribution function

The quantum-mechanical angular pair correlation function for a diatomic molecular fluid is defined as

$$
\rho^2 g(\bar{X}_1,\bar{X}_2)=[(N-2)!\lambda_{\mathrm{tr}}^{3N}\lambda_{\mathrm{rot}}^{2N}Q_N\Omega^{N-2}]^{-1} \times\int\cdots\int W_N(\bar{X}_1,\ldots,\bar{X}_N)\prod_{i=3}^{N}d\bar{X}_i . \tag{2.17}
$$

Substituting Eqs. (2.6)–(2.8) into Eq. (2.17), we obtain an expression for the angular pair correlation function of the diatomic fluid correct to the first order of $\hbar^2$. Thus

$$g(\bar{X}_1,\bar{X}_2)=g^c(\bar{X}_1,\bar{X}_2)+\left[\frac{\hbar^2\beta}{m}\right]g^I_{\mathrm{tr}}(\bar{X}_1,\bar{X}_2)+\left[\frac{\hbar^2\beta}{I}\right]g^I_{\mathrm{rot}}(\bar{X}_1,\bar{X}_2)+O(\hbar^4)\,, \tag{2.18}$$

where $g^I_{\mathrm{tr}}(\bar{X}_1,\bar{X}_2)$ and $g^I_{\mathrm{rot}}(\bar{X}_1,\bar{X}_2)$ are the first-order quantum correction to the pair correlation function due to translational and rotational contribution, respectively.

$g^I_\alpha(\bar{X}_1,\bar{X}_2)$ is given by

$$\begin{aligned}g^I_\alpha(\bar{X}_1,\bar{X}_2)={}&g^c(\bar{X}_1,\bar{X}_2)U^\alpha_2(\bar{X}_1,\bar{X}_2)+\frac{2\rho}{\Omega}\int g^c(\bar{X}_1,\bar{X}_2,\bar{X}_3)U^\alpha_2(\bar{X}_1,\bar{X}_3)d\bar{X}_3\\&+\frac{1}{2}\frac{\rho^2}{\Omega^2}\int[g^c(\bar{X}_1,\bar{X}_2,\bar{X}_3,\bar{X}_4)-g^c(\bar{X}_1,\bar{X}_2)g^c(\bar{X}_3,\bar{X}_4)]U^\alpha_2(\bar{X}_3,\bar{X}_4)d\bar{X}_3\,d\bar{X}_4\\&+\frac{\rho}{\Omega}\int g^c(\bar{X}_1,\bar{X}_2,\bar{X}_3)U^\alpha_3(\bar{X}_1,\bar{X}_2,\bar{X}_3)d\bar{X}_3+\frac{\rho^2}{\Omega^2}\int g^c(\bar{X}_1,\bar{X}_2,\bar{X}_3,\bar{X}_4)U^\alpha_3(\bar{X}_2,\bar{X}_3,\bar{X}_4)d\bar{X}_3\,d\bar{X}_4\\&+\frac{1}{6}\frac{\rho^3}{\Omega^3}\int[g^c(\bar{X}_1,\ldots,\bar{X}_5)-g^c(\bar{X}_1,\bar{X}_2)g^c(\bar{X}_3,\bar{X}_4,\bar{X}_5)]U^\alpha_3(\bar{X}_3,\bar{X}_4,\bar{X}_5)d\bar{X}_3\,d\bar{X}_4\,d\bar{X}_5\,.\end{aligned} \tag{2.19}$$

Here α stands for both tr and rot. $g^c(\bar{X}_1,\ldots,\bar{X}_l)$ is the canonical ensemble l-particle angular distribution function.

III. CLASSICAL MOLECULAR FLUIDS

In this section, we consider the classical fluids of diatomic molecules. The pair potential energy for such a system is given by Eq. (1.2), where $u_0(r_{ij})$ is the central potential between the molecules i and j, and $u_a(\bar{X}_i,\bar{X}_j)$ is the angle-dependent part of pair interaction. For central potential, we take the Lennard-Jones (12-6) potential

$$u_0(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]\,, \tag{3.1}$$

where ϵ and σ are, respectively, the well depth and molecular diameter. For an angle-dependent interaction, we write[10,23–25]

$$\begin{aligned}u_a(\bar{X}_i,\bar{X}_j)={}&u_{\mathrm{quad}}(i,j)+u_{\mathrm{in}}(i,j)\\&+u_{\mathrm{dis}}(i,j)+u_{\mathrm{shape}}(i,j)\,,\end{aligned} \tag{3.2}$$

where u_{quad} is the interaction between the permanent quadrupole moment of the molecules, u_{in} is the interaction of the induced dipole moments in one molecule with the permanent quadrupole moment in the other molecule, u_{dis} is the interaction between anisotropic dispersion forces of the molecules, and u_{shape} is the anisotropy of the short-range overlap forces of molecules. They are expressed as

$$u_{\mathrm{quad}}=\tfrac{3}{4}(\theta^2/r^5)[1-5(\cos^2\theta_1+\cos^2\theta_2)-15\cos^2\theta_1\cos^2\theta_2+2(\sin\theta_1\sin\theta_2\cos\varphi-4\cos\theta_1\cos\theta_2)^2]\,, \tag{3.3a}$$

$$u_{\mathrm{in}}=-\tfrac{9}{8}(\bar{\alpha}\theta^2/r^8)(\sin^4\theta_1+\sin^4\theta_2+4\cos^2\theta_1+4\cos^2\theta_2)\,, \tag{3.3b}$$

$$u_{\mathrm{dis}}=4\epsilon(\sigma/r)^6[K-\tfrac{3}{2}K(1-K)(\cos^2\theta_1+\cos^2\theta_2)-\tfrac{3}{2}K^2(\sin\theta_1\sin\theta_2\cos\varphi-2\cos\theta_1\cos\theta_2)^2]\,, \tag{3.3c}$$

$$u_{\mathrm{shape}}=4\epsilon D(\sigma/r)^{12}(3\cos^2\theta_1+3\cos^2\theta_2-2)\,, \tag{3.3d}$$

where θ_1, θ_2, and φ are the angles which determine the orientation of the molecule with respect to the line joining the centers of the molecules. θ is the quadrupole moment, $\bar{\alpha}$ is the average polarizability, K is the anisotropy in the polarizability, and D is the dimensionless shape parameter of the molecule. The potential parameters ϵ and σ appearing in Eq. (3.3) are characteristic of the Lennard-Jones (12-6) model representing the central potential.

We divide the pair potential $u(\bar{X}_1,\bar{X}_2)$ according to Eq. (1.2), where u_0 is treated as the reference potential and u_a is the perturbation. Using this division of the potential, $g^c(\bar{X}_1,\bar{X}_2)$ can be expanded as[26]

$$g^c(\bar{X}_1,\bar{X}_2)=g^c_0(r_{12})+g^c_1(\bar{X}_1,\bar{X}_2)+\cdots\,, \tag{3.4}$$

where $g^c_0(r_{12})$ is the RDF for the reference system and $g^c_1(\bar{X}_1,\bar{X}_2)$ is the first-order perturbation correction to the RDF of the classical system. The expression for $g^c_1(\bar{X}_1,\bar{X}_2)$ is

$$\begin{aligned}g^c_1(\bar{X}_1,\bar{X}_2)={}&-\beta u_a(\bar{X}_1,\bar{X}_2)g^c_0(r_{12})\\&-\beta\int\langle u_a(\bar{X}_1,\bar{X}_3)+u_a(\bar{X}_2,\bar{X}_3)\rangle_{\omega_3}\\&\times g^c_0(\bar{r}_1,\bar{r}_2,\bar{r}_3)d\bar{r}_3\,,\end{aligned} \tag{3.5}$$

where

$$\langle\cdots\rangle_{\omega_3}=\frac{1}{\Omega}\int(\cdots)d\omega_3\,. \tag{3.6}$$

The corresponding perturbation expansion for the free energy per particle $f^c(=A^c/N)$ of the classical fluid is given by

$$f^c=f^c_0+f^c_1+f^c_2\,, \tag{37}$$

where f^c_0 is the free energy per particle of the reference (classical) fluid and f^c_1 and f^c_2 are, respectively, the first- and second-order perturbation correction to the free energy.

For molecules having the angle-dependent potential [Eq. (3.2)], we have[5]

$$f_1^c = f_1^c(\text{in}) , \tag{3.8}$$

$$\begin{aligned} f_2^c = {} & f_2^c(\text{quad}) + f_2^c(\text{anis-dis}) \\ & + f_2^c(\text{shape}) + f_2^c(\text{quad-in}) + f_2^c(\text{quad-dis}) \\ & + f_2^c(\text{shape-in}) + f_2^c(\text{shape-dis}) , \end{aligned} \tag{3.9}$$

where

$$f_1^c(\text{in}) = -\tfrac{3}{2}[\rho^* \alpha^* (\theta^*)^2 / T^*] \langle (r^*)^{-8} \rangle_2 , \tag{3.10}$$

$$f_2^c(\text{quad}) = -\tfrac{7}{10}[\rho^* (\theta^*)^4 / (T^*)^2] \langle (r^*)^{-10} \rangle_2 , \tag{3.11}$$

$$\begin{aligned} f_2^c(\text{anis-dis}) = {} & -\tfrac{4}{5}[\rho^* / (T^*)^2] \\ & \times [K^2(2 + \tfrac{19}{5}K^2) \langle (r^*)^{-12} \rangle_2 \\ & + 2\rho^* K^2 \langle (r_{12} r_{13})^{-6} P_2(\cos\theta_1) \rangle_3] , \end{aligned} \tag{3.12}$$

$$f_2^c(\text{shape}) = -\tfrac{32}{5}[\rho^* D^2 / (T^*)^2] \langle (r^*)^{-24} \rangle_2 , \tag{3.13}$$

$$f_2^c(\text{quad-in}) = \tfrac{36}{35}[\rho^* \alpha^* (\theta^*)^4 / (T^*)^2] \langle (r^*)^{-13} \rangle_2 , \tag{3.14}$$

$$f_2^c(\text{quad-dis}) = \tfrac{72}{25}[\rho^* K^2 (\theta^*)^2 / (T^*)^2] \langle (r^*)^{-11} \rangle_2 , \tag{3.15}$$

$$f_2^c(\text{shape-in}) = \tfrac{96}{35}[\rho^* \alpha^* (\theta^*)^2 D / (T^*)^2] \langle (r^*)^{-20} \rangle_2 , \tag{3.16}$$

$$f_2^c(\text{shape-dis}) = \tfrac{32}{5}[\rho^* K D / (T^*)^2] \langle (r^*)^{-12} \rangle_2 , \tag{3.17}$$

with

$$\langle (r^*)^{-n} \rangle_2 = \int g_0^c(r^*)(r^*)^{-n} d\bar{r}^* , \tag{3.18}$$

and

$$\langle \cdots \rangle_3 = \int g_0^c(r_{12}^*, r_{13}^*, r_{23}^*)(\cdots) d\bar{r}_2^* d\bar{r}_3^* , \tag{3.19}$$

where $g_0^c(r^*)$ and $g_0^c(r_{12}^*, r_{13}^*, r_{23}^*)$ are, respectively, the two- and three-body distribution functions of the reference (classical) fluid. P_l is the lth Legendre polynomial. In the above expressions we have used the reduced variables defined as

$$\rho^* = \rho\sigma^3 ,$$

$$T^* = kT/\epsilon ,$$

$$\alpha^* = \bar{\alpha}/\sigma^3 ,$$

$$(\theta^*)^2 = \theta^2/\epsilon\sigma^5 ,$$

$$r^* = r/\sigma .$$

Other thermodynamic properties of the classical molecular fluid can be calculated from Eq. (3.7).

We use the Verlet-Weis (VW) method[27] to calculate the thermodynamic properties of the reference [Lennard-Jones (LJ)] system. Thus the free energy per particle of the reference system is given by[27]

$$f_0^c = f_r^c + f_p^c , \tag{3.20}$$

where

$$\beta f_r^c = \beta f_{\text{HS}}^c + 4\beta\delta\Delta f^c \tag{3.21}$$

with

$$\beta f_{\text{HS}}^c = \eta(4 - 3\eta)/(1 - \eta)^2 , \tag{3.22}$$

$$\beta\Delta f^c = 3\eta^2(1 + 1.759\eta - 5.249\eta^3)/(1 - \eta)^3 , \tag{3.23}$$

where

$$\eta = \tfrac{1}{6}\pi\rho^*(d^*)^3 ,$$

$$\rho^* = \rho\sigma^3 ,$$

$$d^* = d/\sigma .$$

Here d is the diameter of a hard sphere and is determined by the expression

$$d = d_B[1 + (\sigma_1/2\sigma_0)\delta] , \tag{3.24}$$

where

$$d_B = \int_0^\infty \{1 - \exp[-\beta u_r(r)]\} dr , \tag{3.25a}$$

$$\delta = \int_0^\infty \left[\frac{r}{d_B} - 1 \right] \frac{d}{dr} \{\exp[-\beta u_r(r)]\} dr , \tag{3.25b}$$

$$\sigma_0 = (1 - \tfrac{1}{2}\eta)/(1 - \eta)^3 , \tag{3.26a}$$

and

$$\sigma_1 = (2 - 7.5\eta + 0.5\eta^2 - 5.7865\eta^3 - 1.51\eta^4)/(1 - \eta)^4 . \tag{3.26b}$$

In Eq. (3.25), $u_r(r)$ represents the reference part of the LJ (12-6) potential according to the perturbation theory of Weeks, Chandler, and Andersen (WCA).[28]

The second term of Eq. (3.20) is the first-order perturbation correction to the free energy and is given by

$$\beta f_p^c = 2\pi\rho \int_d^\infty \omega(r) g_{\text{HS}}^c(r) r^2 dr , \tag{3.27}$$

where $g_{\text{HS}}^c(r)$ is the RDF of the classical hard-sphere fluid of diameter d and $w(r)$ is defined as

$$w(r) = \begin{cases} -\epsilon, & r < r_m \\ u_{\text{LJ}}(r), & r > r_m . \end{cases} \tag{3.28}$$

r_m is the distance at which $u_{\text{LJ}}(r) = -\epsilon$. Using the standard relations one can calculate the other thermodynamic properties from the free energy of the reference system.

IV. QUANTUM CORRECTION TO THERMODYNAMIC PROPERTIES

The first-order quantum correction to the free energy is expressed in terms of the classical RDF $g^c(\bar{X}_1, \bar{X}_2)$. In terms of the reduced quantities

$$\Lambda^* = \frac{h}{\sigma\sqrt{m\epsilon}} ,$$

$$\delta^* = \frac{h}{\sqrt{I\epsilon}} ,$$

Eq. (2.14) can be written as

$$\beta f = \beta f^c + (\Lambda^*)^2 (f_{\text{tr}}^I)^* + (\delta^*)^2 (f_{\text{rot}}^I)^* , \tag{4.1}$$

where

$$(f_{\text{tr}}^I)^* = \frac{\rho^*}{768\pi^3(T^*)^2} \int g^c(\bar{X}_1,\bar{X}_2) \left[\frac{1}{(r^*)^2} \frac{\partial}{\partial r^*} \left[(r^*)^2 \frac{\partial u^*(\bar{X}_1,\bar{X}_2)}{\partial r^*} \right] \right] d\bar{r}^*\, d\omega \;, \tag{4.2}$$

$$(f_{\text{rot}}^I)^* = \frac{\rho^*}{768\pi^3(T^*)^2} \int g^c(\bar{X}_1,\bar{X}_2) \left[\frac{1}{\sin\theta_1} \frac{\partial}{\partial \theta_1} \left[\sin\theta_1 \frac{\partial u^*(\bar{X}_1,\bar{X}_2)}{\partial \theta_1} \right] + \frac{1}{\sin^2\theta_1} \frac{\partial^2 u^*(\bar{X}_1,\bar{X}_2)}{\partial \varphi_1^2} \right] d\bar{r}^*\, d\omega \;. \tag{4.3}$$

Here $u^*(\bar{X}_1,\bar{X}_2)=u(\bar{X}_1,\bar{X}_2)/\epsilon$.

Using Eqs. (3.2) and (3.5) in Eq. (4.2), the first-order quantum correction to the free energy per particle due to translational contribution is given by

$$\begin{aligned}(f_{\text{tr}}^I)^* = {}& [f_{\text{tr}}^I(\text{LJ})]^* + [f_{\text{tr}}^I(\text{in})]^* + [f_{\text{tr}}^I(\text{quad})]^* + [f_{\text{tr}}^I(\text{anis-dis})]^* + [f_{\text{tr}}^I(\text{shape})]^* \\ & + [f_{\text{tr}}^I(\text{quad-dis})]^* + [f_{\text{tr}}^I(\text{quad-dis})]^* + [f_{\text{tr}}^I(\text{shape-in})]^* + [f_{\text{tr}}^I(\text{shape-dis})]^* \;,\end{aligned} \tag{4.4}$$

where

$$[f_{\text{tr}}^I(\text{LJ})]^* = \frac{1}{4\pi^2}[\rho^*/(T^*)^2][22\langle (r^*)^{-14}\rangle_2 - 5\langle (r^*)^{-8}\rangle_2] \;, \tag{4.5}$$

$$[f_{\text{tr}}^I(\text{in})]^* = -\frac{3}{4\pi^2}[\rho^*\alpha^*(\theta^*)^2/(T^*)^2][\tfrac{7}{3}\langle (r^*)^{-10}\rangle_2 - \frac{1}{T^*}(22\langle (r^*)^{-22}\rangle_2 - 5\langle (r^*)^{-16}\rangle_2)] \;, \tag{4.6}$$

$$[f_{\text{tr}}^I(\text{quad})]^* = -\frac{7}{24\pi^2}[\rho^*(\theta^*)^4/(T^*)^3]\langle (r^*)^{-12}\rangle_2 \;, \tag{4.7}$$

$$[f_{\text{tr}}^I(\text{anis-dis})]^* = -\frac{1}{2\pi^2}[\rho^*/(T^*)^3][K^2(2+\tfrac{19}{5}K^2)\langle (r^*)^{-14}\rangle_2 + 2\rho^* K^2 \langle [(r_{12}^*)^{-8}(r_{13}^*)^{-6}]P_2(\cos\theta_1)\rangle_3] \;, \tag{4.8}$$

$$[f_{\text{tr}}^I(\text{shape})]^* = -\frac{88}{5\pi^2}[\rho^* D^2/(T^*)^3]\langle (r^*)^{-26}\rangle_2 \;, \tag{4.9}$$

$$[f_{\text{tr}}^I(\text{quad-in})]^* = \frac{57}{70\pi^2}[\rho^*\alpha^*(\theta^*)^4/(T^*)^3]\langle (r^*)^{-15}\rangle_2 \;, \tag{4.10}$$

$$[f_{\text{tr}}^I(\text{quad-dis})]^* = \frac{3}{2\pi^2}[\rho^* K^2(\theta^*)^2/(T^*)^3]\langle (r^*)^{-13}\rangle_2 \;, \tag{4.11}$$

$$[f_{\text{tr}}^I(\text{shape-in})]^* = \frac{188}{35\pi^2}[\rho^*\alpha^*(\theta^*)^2 D/(T^*)^3]\langle (r^*)^{-22}\rangle_2 \;, \tag{4.12}$$

$$[f_{\text{tr}}^I(\text{shape-dis})]^* = \frac{54}{5\pi^2}[\rho^* KD/(T^*)^3]\langle (r^*)^{-20}\rangle_2 \;. \tag{4.13}$$

Similarly, the first-order quantum correction to the free energy per particle due to rotational contribution is given by

$$\begin{aligned}(f_{\text{rot}}^I)^* = {}& [f_{\text{rot}}^I(\text{quad})]^* + [f_{\text{rot}}^I(\text{in})]^* + [f_{\text{rot}}^I(\text{anis-dis})]^* + [f_{\text{rot}}^I(\text{shape})]^* \\ & + [f_{\text{rot}}^I(\text{quad-in})]^* + [f_{\text{rot}}^I(\text{quad-dis})]^* + [f_{\text{rot}}^I(\text{quad-shape})]^* + [f_{\text{rot}}^I(\text{in-dis})]^* \\ & + [f_{\text{rot}}^I(\text{shape-in})]^* + [f_{\text{rot}}^I(\text{shape-dis})]^* \;,\end{aligned} \tag{4.14}$$

where

$$[f_{\text{rot}}^I(\text{quad})]^* = \frac{119}{768\pi^2}[\rho^*(\theta^*)^4/(T^*)^3]\langle (r^*)^{-10}\rangle_2 \;, \tag{4.15}$$

$$[f_{\text{rot}}^I(\text{in})]^* = \frac{33}{560\pi^2}[\rho^*(\alpha^*)^2(\theta^*)^4/(T^*)^3]\langle (r^*)^{-16}\rangle_2 \;, \tag{4.16}$$

$$[f_{\text{rot}}^I(\text{anis-dis})]^* = \frac{1}{5\pi^2}[\rho^*/(T^*)^3]K(1+\tfrac{13}{5}K^2)\langle (r^*)^{-12}\rangle_2 \;, \tag{4.17}$$

$$[f_{\text{rot}}^I(\text{shape})]^* = -\frac{4}{5\pi^2}[\rho^* D^2/(T^*)^3]\langle (r^*)^{-24}\rangle_2 \;, \tag{4.18}$$

$$[f_{\text{rot}}^I(\text{quad-in})]^* = -\frac{523}{4480\pi^2}\left[\frac{\rho^*\alpha^*(\theta^*)^4}{(T^*)^3}\right]\langle (r^*)^{-13}\rangle_2 \;, \tag{4.19}$$

$$[f_{\text{rot}}^I(\text{quad-dis})]^* = -\frac{1}{48\pi^2}[\rho^*(\theta^*)^2/(T^*)^3]K(1+\tfrac{153}{5}K)\langle (r^*)^{-11}\rangle_2 \;, \tag{4.20}$$

TABLE I. Force parameters used in the present calculations.

System	ϵ/k (K)	σ (Å)	$10^{24}\bar{\alpha}$ (cm^2)	$10^{26}\theta$ (esu cm^2)	K	D	Λ^*	δ^*
D_2	35.0	2.976	0.7954	0.84	0.1153	0.21	1.238	9.9358
H_2	37.0	2.928	0.790	0.84	0.0911	0.21	1.729	13.4997

$$[f^I_{\rm rot}(\text{quad-shape})]^* = -\frac{7}{24\pi^2}[\rho^*(\theta^*)^2 D/(T^*)^3]\langle (r^*)^{-17}\rangle_2 \,, \tag{4.21}$$

$$[f^I_{\rm rot}(\text{in-dis})]^* = \frac{3}{224\pi^2}\left[\frac{\rho^*\alpha^*(\theta^*)^2}{(T^*)^3}\right]K^2\langle (r^*)^{-14}\rangle_2 \,, \tag{4.22}$$

$$[f^I_{\rm rot}(\text{shape-in})]^* = -\frac{9}{80\pi^2}\left[\frac{\rho^*\alpha^*(\theta^*)^2 D}{(T^*)^3}\right]\langle (r^*)^{-20}\rangle_2 \,, \tag{4.23}$$

$$[f^I_{\rm rot}(\text{shape-dis})]^* = -\frac{7}{15\pi^2}\left[\frac{\rho^* D}{(T^*)^2}\right]K(1-\tfrac{3}{14}K)\langle (r^*)^{-18}\rangle_2 \,. \tag{4.24}$$

Other thermodynamic properties can be calculated from Eq. (4.1). Thus the equation of state is given by

$$\frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} + (\Lambda^*)^2(P^I_{\rm tr})^* + (\delta^*)^2(P^I_{\rm rot})^* \,, \tag{4.25}$$

where

$$(P^I_{\rm tr})^* = \rho^*\frac{\partial (f^I_{\rm tr})^*}{\partial \rho^*} \,, \tag{4.26a}$$

$$(P^I_{\rm rot})^* = \rho^*\frac{\partial (f^I_{\rm rot})^*}{\partial \rho^*} \,. \tag{4.26b}$$

The coefficients $(P^I_{\rm tr})^*$ and $(P^I_{\rm rot})^*$ are the first-order quantum correction to the pressure due to the translational and rotational contributions, respectively. The entropy S and the internal energy U, correct to the first-order quantum correction, are given by

$$\frac{S}{NK} = \frac{S^c}{NK} + (\Lambda^*)^2(S^I_{\rm tr})^* + (\delta^*)^2(S^I_{\rm rot})^* \,, \tag{4.27}$$

where

$$(S^I_{\rm tr})^* = -\frac{\partial}{\partial T^*}\left[T^*\frac{\partial (f^I_{\rm tr})^*}{\partial T^*}\right] , \tag{4.28a}$$

$$(S^I_{\rm rot})^* = -\frac{\partial}{\partial T^*}\left[T^*\frac{\partial (f^I_{\rm rot})^*}{\partial T^*}\right] , \tag{4.28b}$$

and

$$\frac{U}{NkT} = \frac{U^c}{NkT} + (\Lambda^*)^2(U^I_{\rm tr})^* + (\delta^*)^2(U^I_{\rm rot})^* \tag{4.29}$$

with

$$(U^I_{\rm tr})^* = -T^*\frac{\partial (f^I_{\rm tr})^*}{\partial T^*} \,, \tag{4.30a}$$

$$(U^I_{\rm rot})^* = -T^*\frac{\partial (f^I_{\rm rot})^*}{\partial T^*} \,. \tag{4.30b}$$

V. RESULTS AND DISCUSSION

In this section, we use the theory developed in the previous section to calculate the thermodynamic properties of diatomic molecules such as D_2 and H_2, where the quantum effects are appreciable. Force parameters for these systems are given in Table I. The parameters θ and D, which are assumed to be the same for H_2 and D_2, are

TABLE II. First-order quantum correction coefficient for free energy and pressure of D_2.

	Free energy				Pressure			
Contributions	$\rho^*=0.85$ $(f^I_{\rm tr})^*$	$T^*=2.74$ $(f^I_{\rm rot})^*$	$\rho^*=0.65$ $(f^I_{\rm tr})^*$	$T^*=1.35$ $(f^I_{\rm rot})^*$	$\rho^*=0.85$ $(P^I_{\rm tr})^*$	$T^*=2.74$ $(P^I_{\rm rot})^*$	$\rho^*=0.65$ $(P^I_{\rm tr})^*$	$T^*=1.35$ $(P^I_{\rm rot})^*$
LJ	0.087 50		0.315 18		0.046 63		0.449 36	
quad	−0.000 66	0.000 51	−0.008 01	0.005 22	0.000 37	−0.000 01	−0.009 29	0.006 04
in	0.004 62	0.0	0.011 50	0.0	0.012 92	−0.0	0.024 47	0.0
anis-dis	−0.000 16	0.000 02	−0.000 97	0.000 19	−0.000 20	−0.000 01	−0.001 36	0.000 22
shape	−0.001 28	−0.000 29	−0.029 84	−0.001 82	0.004 10	−0.000 15	−0.031 21	−0.002 72
quad-in	0.000 02	−0.000 03	0.000 48	−0.000 11	−0.000 05	−0.000 06	0.000 44	−0.000 17
quad-dis	0.000 24	−0.000 13	0.001 02	−0.000 63	0.000 55	−0.000 26	0.001 57	0.000 93
quad-shape	0.0	−0.000 24	0.0	−0.002 17	0.0	0.0	0.0	−0.002 85
shape-in	0.000 38	−0.0	0.001 29	−0.000 02	0.000 86	0.0	0.002 22	−0.000 02
shape-dis	0.000 56	−0.000 02	0.011 32	−0.000 49	−0.001 44	0.000 06	0.012 17	−0.000 50
Total	0.091 22	−0.000 19	0.301 94	0.000 17	0.063 72	−0.000 42	0.448 36	−0.000 93

TABLE III. Free energy and pressure of D_2.

	Free energy				Pressure			
	$\rho^*=0.85$	$T^*=2.74$	$\rho^*=0.65$	$T^*=135$	$\rho^*=0.85$	$T^*=2.74$	$\rho^*=0.65$	$T^*=1.35$
Contributions	βf^c	βf	βf^c	βf	$\beta P^c/\rho$	$\beta P/\rho$	$\beta P^c/\rho$	$\beta P/\rho$
LJ	−0.8595	−0.7253	1.2446	1.7277	4.2896	4.3611	0.6050	1.2937
in	−0.0550	−0.0479	−0.0647	−0.0470	−0.1104	−0.0906	−0.0886	−0.0510
quad	−0.0620	−0.0129	−0.3143	0.1889	0.0014	0.0008	−0.3635	0.2185
anis-dis	−0.0034	−0.0021	−0.0204	−0.0028	0.0019	0.0007	−0.0236	−0.0036
shape	−0.0624	−0.0929	−0.1940	−0.4194	−0.0314	−0.0395	−0.2904	−0.6071
quad-in	0.0064	0.0038	0.0133	−0.0028	0.0145	0.0084	0.0203	0.0039
quad-dis	0.0124	−0.0001	0.0294	−0.0310	0.0243	−0.0001	0.0436	−0.0458
quad-shape	0.0	−0.0237	0.0	−0.2146	0.0	0.0001	0.00	−0.2815
shape-in	0.0006	0.0011	0.0063	−0.0063	−0.0016	−0.0001	0.0067	0.0081
shape-dis	0.0081	0.0069	0.0923	0.0610	−0.0210	−0.0177	0.0928	0.0626
Total	−1.0147	−0.8932	0.7925	1.2720	4.1672	4.2231	0.0024	0.5977

determined by Singh and Datta[22] and by de Boer,[29] respectively. The values of $\bar{\alpha}, K$, and δ^* for D_2 are given by Kolos and Wolniewiez.[30] For H_2, $\bar{\alpha}$ and K are determined by Volkmann,[31] while δ^* is obtained from the value of $\hbar^2/2kI$.[32]

We have calculated the first-order quantum correction to the thermodynamic properties due to the translational and rotational contributions. The integral $\langle (r^*)^{-n} \rangle_2$ that appears in the expressions of the thermodynamic properties can be written as

$$\langle (r^*)^{-n} \rangle_2 = 4\pi J_n \ , \tag{5.1}$$

where J_n is evaluated using the empirical equation of Ananth,[33]

$$\ln J_n(\rho^*, T^*) = A_n(\rho^*)^2 \ln T^* + B_n(\rho^*)^2 + C_n \rho^* \ln T^* + D_n \rho^* + E_n \ln T^* + F_n \ . \tag{5.2}$$

The constants $A_n - F_n$ are reported by Gray and Gubbins.[34]

The contributions of the various branches of pair interactions to the first-order quantum correction coefficients for the free energy and pressure of D_2 are reported in Table II at $\rho^*=0.85$, $T^*=2.74$ and $\rho^*=0.65$, $T^*=1.35$. It is seen from the table that the rotational contribution is very small in comparison to the translational contribution. In the translational part, the main contribution arises from the central force, i.e., the LJ (12-6) potential. The table demonstrates the magnitude of the contribution of various branches of nonspherical interactions.

Table III demonstrates the magnitude of contribution of the different pair potentials to the free energy per particle and pressure of D_2 at $\rho^*=0.85$, $T^*=2.74$ and $\rho^*=0.65$, $T^*=1.35$. The classical values are also shown in the table. We see that the main contribution comes from the LJ potential and that the contribution of the nonspherical parts is small and increases with the decrease in temperature. Among the nonspherical interactions, the most significant contributions arise from quadrupole moment and shape interactions as well as the cross term arising from quadrupole moment and shape. The contribution of other terms is found to be small but not negligible.

The calculated values of thermodynamic properties such as the free energy per particle, internal energy, and pressure are given in Tables IV and V for D_2 and H_2, respectively. It may be seen from these tables that the quantum effect to the thermodynamic properties increases with the increase of density and decrease in temperature. Further, we see that the quantum effect is small at $T^*=2.74$, where the contribution of nonspherical interaction is also small. As the temperature decreases, the contribution of both the quantum effect and nonspherical interaction increases. At $T^*=0.75$ the quantum effect is very large. One should include at least the second-order quantum correction before predicting the thermodynamic properties at low temperature.

TABLE IV. Thermodynamic properties of D_2.

		Free energy		Internal energy		Pressure	
ρ^*	T^*	βf^c	βf	U^c/NkT	U/NkT	$\beta P^c/\rho$	$\beta P/\rho$
0.50	2.74	−0.1730	−0.0899	−2.4507	−2.6106	1.3274	1.6158
0.50	1.35	0.7563	1.1172	3.8538	4.6481	−0.2272	0.1195
0.50	0.75	2.0833	3.6068	−5.2920	−9.3144	−3.3340	−1.8184
0.65	2.74	−0.4053	−0.3032	−3.9471	−4.1565	2.0499	2.1241
0.65	1.35	0.7925	1.2720	−5.1963	−6.2781	0.0024	0.5977
0.65	0.75	2.5018	4.5331	−7.1350	−12.3915	−4.6838	−3.4225
0.85	2.74	−1.0147	−0.8932	−4.7859	−5.0909	4.1672	4.2231
0.85	1.35	0.3377	1.0570	−6.0702	−7.7819	1.7474	3.0859
0.85	0.75	2.0751	4.7821	−10.8474	−15.7891	−5.9811	−4.5501

TABLE V. Thermodynamic properties of H_2.

		Free energy		Internal energy		Pressure	
ρ^*	T^*	βf^c	βf	U^c/NkT	U/NkT	$\beta P^c/\rho$	$\beta P/\rho$
0.50	2.74	−0.1807	−0.0113	−2.4652	−2.7968	1.3212	1.8907
0.50	1.35	0.7245	1.4814	−3.9211	−5.6185	−0.2590	0.4750
0.50	0.75	1.9690	5.2261	−5.5468	−14.2117	−0.4789	−0.1633
0.65	2.74	−0.4146	−0.2059	−3.9652	−4.4000	2.0433	2.1978
0.65	1.35	0.7503	1.7590	−5.2935	−7.6174	−0.0474	1.2200
0.65	0.75	2.3280	6.7215	−7.5269	−19.0976	−5.0344	−1.6839
0.85	2.74	−1.0261	−0.7760	−4.8084	−5.4418	4.1558	4.2850
0.85	1.35	0.2771	1.7982	−6.2367	−9.9502	1.6523	4.5195
0.85	0.75	1.7139	7.8743	−12.0358	−24.8757	−7.2980	−1.3896

VI. CONCLUDING REMARKS

In this paper, we have estimated the quantum effect due to the various branches of pair interactions to the thermodynamic properties of the diatomic molecules such as D_2 and H_2. We have considered only the first-order quantum correction. This approximation may be valid at high temperature. At low temperature, one should consider the higher-order corrections to get better results. But the exact evaluation of even the second-order correction is very difficult, so we have not attempted to here. We have used the perturbation theory, in which all the nonspherical interactions are taken as perturbation, to calculate the thermodynamic properties of the classical molecular fluids.

In conclusion, we feel that this theory is appropriate to calculate the thermodynamic properties of molecular fluids at high temperatures, where the quantum effects are small and the series is truncated after the first-order quantum correction term.

---

[*] Permanent address: Department of Physics, S. R. K. Goenka College, Bihar University, Sitamarhi 843301, Bihar, India.

[1] See, for example, *Molecular-Based Study of Fluids,* edited by J. M. Haile and G. A. Mansoori (American Chemical Society, New York, 1983).

[2] Y. Singh and S. K. Sinha, Phys. Rep. 79, 215 (1981).

[3] Y. Singh, Mol. Phys. 29, 155 (1975).

[4] K. P. Shukla, J. Ram, and Y. Singh, Mol. Phys. 31, 873 (1976).

[5] K. P. Shukla, S. Singh, and Y. Singh, J. Chem. Phys. 70, 3086 (1979).

[6] M. S. Ananth, K. E. Gubbins, and C. G. Gray, Mol. Phys. 28, 1005 (1974).

[7] M. Flytzanis-Stephanopoulos, K. E. Gubbins, and C. G. Gray, Mol. Phys. 30, 1649 (1975).

[8] B. M. Ladanyi and D. Chandler, J. Chem. Phys. 62, 4308 (1975).

[9] K. C. Mo and K. E. Gubbins, J. Chem. Phys. 63, 1490 (1975).

[10] W. R. Smith, Chem. Phys. Lett. 40, 313 (1976).

[11] R. L. Henderson and C. G. Gray, Can. J. Phys. 56, 571 (1978).

[12] S. I. Sandler, Mol. Phys. 28, 1207 (1974).

[13] S. S. Wang, C. G. Gray, P. A. Egelstaff, and K. E. Gubbins, Chem. Phys. Lett. 21, 123 (1973); 24, 453 (1974).

[14] G. Stell, J. C. Rasaiah, and H. Narang, Mol. Phys. 27, 1393 (1974).

[15] P. T. Cummings and G. Stell, Mol. Phys. 46, 383 (1982).

[16] J. de Boer and R. B. Bird, in *Molecular Theory of Gases and Liquids,* edited by J. O. Hirschfelder, C. F. Curtis, and R. B. Bird (Wiley, New York, 1954), Chap. 6.

[17] E. Wigner, Phys. Rev. 40, 749 (1932).

[18] J. G. Kirkwood, Phys. Rev. 44, 31 (1933).

[19] For a recent review, see Ref. 2.

[20] H. Friedmann, Adv. Chem. Phys. 4, 225 (1962).

[21] C. S. Wang Chang, Ph.D. dissertation, University of Michigan, 1944.

[22] Y. Singh and K. K. Datta, J. Chem. Phys. 53, 1189 (1970).

[23] J. A. Pople, Proc. R. Soc. London, Ser. A 221, 508 (1954).

[24] S. Kielech, Acta Phys. Pol. 20, 433 (1961); Physica (Utrecht) 35, 1675 (1961).

[25] R. H. Orcutt, J. Chem. Phys. 39, 605 (1963).

[26] K E. Gubbins and C. G. Gray, Mol. Phys. 23, 187 (1972).

[27] L. Verlet and J. J. Weis, Phys. Rev. A 5, 939 (1972); Mol. Phys. 24, 1013 (1972).

[28] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. 54, 5237 (1971).

[29] J. de Boer, Physica (Utrecht) 9, 363 (1942).

[30] W. Kolos and L. Wolniewiez, J. Chem. Phys. 46, 1426 (1967).

[31] H. Volkmann, Ann. Phys. (Leipzig) 24, 457 (1935).

[32] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1970), p. 131.

[33] M. S. Ananth, Ph.D. dissertation, University of Florida, 1972.

[34] C. G. Gray and K. E. Gubbins, Mol. Phys. 30, 179 (1975).