

## Equilibrium properties of molecular fluids in the semiclassical limit. II. Hydrogen molecules

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(Received 18 March 1986)

Thermodynamic properties, such as pressure entropy and configurational energy, of fluid H<sub>2</sub> are evaluated where the first-order quantum correction is taken into account. Agreement for the pressure and entropy is found to be good at high temperature ( $T \geq 100$  K).

### I. INTRODUCTION

In the previous paper<sup>1</sup> (which we refer to as I) we have developed a theory for calculating the quantum correction to the thermodynamic properties of molecular fluids of diatomic molecules. This is based on the assumption that the total interaction potential is pairwise additive, i.e.,

$$U(\mathbf{X}_1, \dots, \mathbf{X}_N) = \sum_{1 \leq i < j \leq N} u(\mathbf{X}_i, \mathbf{X}_j), \quad (1)$$

where  $u(\mathbf{X}_i, \mathbf{X}_j)$  is the pair potential between molecules  $i$  and  $j$  and the vector  $\mathbf{X}_i = (\mathbf{r}_i, \omega_i)$  represents both the position of the center of mass and orientation of the  $i$ th molecule. The pair potential model is assumed to be of the form

$$u = u_{LJ} + u_{QQ} + u_{in} + u_{dis} + u_{shape}, \quad (2)$$

where  $u_{LJ}$  is the Lennard-Jones (LJ) (12-6) potential,  $u_{QQ}$  is the permanent quadrupole-quadrupole potential,  $u_{in}$  is the induced dipole-permanent quadrupole potential,  $u_{dis}$  is the anisotropic dispersion potential, and  $u_{shape}$  is anisotropic short-range overlap potential. However, the calculated results could not be compared with any experimental values. Further, in the derivation of paper I, we have treated the single-molecule rotational partition function classically. Although it will not affect the configurational energy and pressure,<sup>2</sup> it should be taken correctly into account while dealing with the total energy.

We may adopt this approach to calculate the thermodynamic properties of fluid of hydrogen molecules (H<sub>2</sub>). Although the quantum effects for hydrogen are large,<sup>3,4</sup> they can be treated semiclassically because the quantum effects for them can be treated as a correction at high temperature.<sup>3</sup>

Powles and Rickayzen<sup>5</sup> have also calculated the quantum correction to the free energy and pressure in terms of  $\langle F^2 \rangle$  and  $\langle \tau^2 \rangle$ , where  $\langle F^2 \rangle$  and  $\langle \tau^2 \rangle$  are the classical mean-squared force and mean-square torque of a molecule, respectively. However, their study is confined to a few molecular fluids, where quantum effects are small. Clancy and Gubbins<sup>3</sup> have estimated the first-order quantum correction for hydrogen. However, they have not taken  $u_{in}$  into account. Its contribution is not expected to be negligible.

In this paper we treat the single-molecule rotational

partition function semiclassically and include  $u_{in}$  to calculate the thermodynamic properties of H<sub>2</sub>.

### II. THEORETICAL BASIS

We consider fluids of diatomic molecules which are permanently in their ground electronic and ground vibrational states. In the quantum statistical mechanics, the canonical partition function is defined as

$$Q_N = (N! \lambda_i^{3N} q_r^{-N} \Omega^N)^{-1} \times \int \cdots \int W_N(\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_N) \prod_{i=1}^N d\mathbf{X}_i, \quad (3)$$

where  $d\mathbf{X}_i = d\mathbf{r}_i d\omega_i$ ,  $\Omega = 4\pi$  for linear molecules, and  $W_N$  is the Slater sum which may be defined in this case as

$$W_N(\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_N) = N! \lambda_i^{3N} q_r^{-N} \sum_x \psi_x^* \exp(-\beta \hat{H}_N) \psi_x, \quad (4)$$

$$\lambda_i = (2\pi \hbar^2 \beta / m)^{1/2}, \quad (5)$$

$$q_r = \sum_J (2J+1) \exp[-\beta J(J+1) \hbar^2 / 2I] \quad (6)$$

[ $m$  is mass,  $I$  is the moment of inertia of a molecule, and  $\beta = (kT)^{-1}$ ]. In Eq. (4)  $\psi_x$ 's are a complete set of orthonormal  $N$  particle wave functions. The summation in Eq. (4) extends over all states.  $\hat{H}_N$  is the Hamiltonian of the system

$$\hat{H}_N = -\frac{\hbar^2}{2m} \nabla_i^2 + U, \quad (7)$$

where  $\nabla_i^2$  is the generalized Laplacian operator in an  $s$ -dimensional space.  $q_r$  is the single-molecule rotational partition function.

In the semiclassical limit, where the quantum effects are small,  $q_r$  for linear molecules is given by<sup>2</sup>

$$q_r = \lambda_r^{-2} \left[ 1 + \frac{1}{6} \left[ \frac{\beta \hbar^2}{I} \right] \right], \quad (8)$$

where

$$\lambda_r^{-2} = (\beta \hbar^2 / 2I) \quad (9)$$

is the classical value for the single-molecule rotational partition function. The expansion of the Slater sum in the

order of  $\hbar^2$  is given in paper I.

The corresponding expression for the Helmholtz free energy is given as

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} + \left[ \frac{\hbar^2 \beta}{m} \right] \left[ \frac{A_{\text{tr}}^I}{N} \right] + \left[ \frac{\hbar^2 \beta}{I} \right] \left[ \frac{A_{\text{rot}}^I}{N} \right] - \left[ \frac{\hbar^2 \beta}{6I} \right] + O(\hbar^4), \quad (10)$$

where  $A^c$  is the free energy for the classical fluid. The first-order quantum correction contains three terms—the first two arise from the translational and rotational potential energy effects, respectively, while the last term in Eq. (10) is due to the rotational kinetic energy. The first two terms of first-order quantum correction are reported in paper I.

For calculating the thermodynamic properties of  $\text{H}_2$  we consider the pair potential energy given in Eq. (2). For such a system, in terms of the reduced quantities

$$\Lambda^* = h/\sigma(m\epsilon)^{1/2},$$

$$\delta^* = h/(I\epsilon)^{1/2}.$$

Equation (10) can be written as

$$\beta f = \beta f^c + \Lambda^{*2} (f_{\text{tr}}^I)^* + \delta^{*2} (f_{\text{rot}}^I)^* - \frac{\delta^{*2}}{24\pi^2 T^*}, \quad (11)$$

$$(f_{\text{tr}}^I)^* = [f_{\text{tr}}^I(\text{LJ})]^* + [f_{\text{tr}}^I(\text{in})]^* + [f_{\text{tr}}^I(\text{quad})]^* + [f_{\text{tr}}^I(\text{anis-dis})]^* + [f_{\text{tr}}^I(\text{shape})]^* + [f_{\text{tr}}^I(\text{dis-in})]^* + [f_{\text{tr}}^I(\text{quad-dis})]^* + [f_{\text{tr}}^I(\text{shape-in})]^* + [f_{\text{tr}}^I(\text{shape-dis})]^*, \quad (15)$$

$$(f_{\text{rot}}^I)^* = [f_{\text{rot}}^I(\text{quad})]^* + [f_{\text{rot}}^I(\text{in})]^* + [f_{\text{rot}}^I(\text{anis-dis})]^* + [f_{\text{rot}}^I(\text{shape})]^* + [f_{\text{rot}}^I(\text{quad-in})]^* + [f_{\text{rot}}^I(\text{quad-dis})]^* + [f_{\text{rot}}^I(\text{quad-shape})]^* + [f_{\text{rot}}^I(\text{dis-in})]^* + [f_{\text{rot}}^I(\text{shape-in})]^* + [f_{\text{rot}}^I(\text{shape-dis})]^*. \quad (16)$$

These are reported in paper I. However, there are some misprints in Eqs. (4.4)–(4.24) of paper I, and corrected versions are given in Appendixes A and B. Other thermodynamic properties can be calculated from Eq. (11) using the standard thermodynamic relations of paper I.

### III. RESULTS AND DISCUSSIONS

In this section we calculate the thermodynamic properties of  $\text{H}_2$  where the quantum effects are appreciable. The force parameters for these systems are given in Table I. We chose those parameters with which calculations have been made earlier by Clancy and Gubbins.<sup>3</sup>

We have calculated the first-order quantum correction to the thermodynamic properties. We use the empirical equation of Ananth<sup>7</sup> to evaluate the integral  $\langle (r^*)^{-n} \rangle_2$  appearing in the expressions of the thermodynamic properties.

The contribution of the various branches of pair interaction potentials to the excess free energy per particle and pressure are reported in Table II at  $\rho^* = 0.22638$ ,  $T^* = 2.16$ , and  $\rho^* = 0.45844$ ,  $T^* = 3.24$ . The classical

where  $T^* = kT/\epsilon$  and  $f = A/N$  is the free energy per particle.

For the free energy per particle  $f^c$  of the classical fluid, we have

$$f^c = f_0^c + f_1^c + f_2^c, \quad (12)$$

where  $f_0^c$  is the free energy per particle of the classical reference fluid and  $f_1^c$  and  $f_2^c$  are, respectively, the first- and second-order perturbation correction to the free energy,<sup>6</sup>

$$f_1^c = f_1^c(\text{in}), \quad (13)$$

$$f_2^c = f_2^c(\text{quad}) + f_2^c(\text{anis-dis}) + f_2^c(\text{shape}) + f_2^c(\text{dis-in}) + f_2^c(\text{quad-dis}) + f_2^c(\text{shape-in}) + f_2^c(\text{shape-dis}). \quad (14)$$

For details, we refer to paper I. There are some misprints in Eqs. (3.10)–(3.17) of paper I:  $\beta$  is missing from the right-hand side of these equations and Eq. (3.14) of paper I should be read as

$$\beta f_2^c(\text{dis-in}) = -\frac{48}{35} [\rho^* \alpha^* (\theta^*)^2 K / (T^*)^2] \langle (r^*)^{-14} \rangle_2.$$

In Eq. (11),  $(f_{\text{tr}}^I)^*$  and  $(f_{\text{rot}}^I)^*$  are the first-order quantum corrections to the free energy due to the translational and rotational contribution, respectively, and they are given by

values are also shown in Table II. We see that the contribution of  $u_{\text{in}}$ , which increases with the increase of density and decrease of temperature, is small but not negligible and should be taken into account.

The quantum corrections to the configurational energy, entropy, and pressure for fluid  $\text{H}_2$  have been calculated and are shown in Table III. We find that the quantum effects increase with the increase of density and decrease of temperature. We have also estimated the contribution of the rotational potential energy to the first-order quantum correction to the configurational energy and pressure. The contributions of rotational part to the quantum correction are found to increase with the increase of density and decrease of temperature. For example, for pressure at  $\rho = 9.468 \text{ mol l}^{-1}$ , its contribution is 21.22% at  $T = 120 \text{ K}$  and 31.71% at  $T = 80 \text{ K}$ , while at  $\rho = 30.322 \text{ mol l}^{-1}$ , the corresponding values are 24.40% and 34.55% at  $T = 120$  and  $80 \text{ K}$ , respectively.

The compressibility and entropy of the fluid  $\text{H}_2$  are calculated including, as well as excluding, the induced interaction,  $u_{\text{in}}$ . They are reported in Table IV. The experimental results<sup>8</sup> are also demonstrated in Table IV. Again

TABLE I. Force parameters of H<sub>2</sub> used in the present calculations.

$\epsilon/k$ (K)	$\sigma$ (Å)	$10^{24}\alpha$ (cm <sup>3</sup> )	$10^{26}\theta$ (esu)	K	D	$\Lambda^*$	$\delta^*$
37.0	2.928	0.806	0.65	0.125	0.1	1.729	13.4997

TABLE II. Contribution to the configurational free energy and pressure of fluid H<sub>2</sub>.

Contributions	$\rho^*=0.22638$	$T^*=2.16$	$\rho^*=0.45844$	$T^*=3.24$	$\rho^*=0.22638$	$T^*=2.16$	$\rho^*=0.45844$	$T^*=3.24$
	$\beta f^c$	$\beta f$	$\beta f^c$	$\beta f$	$\beta P^c/\rho$	$\beta P/\rho$	$\beta P^c/\rho$	$\beta P/\rho$
LJ	-0.15430	0.00101	0.18202	0.34991	0.85921	1.00360	1.44780	1.68301
In	-0.00964	-0.00695	-0.01290	-0.01116	-0.00856	-0.00686	-0.01344	-0.01198
quad	-0.01564	0.03501	-0.01654	0.01793	-0.01720	0.03843	-0.02484	0.02760
anis-dis	-0.00310	-0.00036	-0.00360	-0.00141	-0.00365	-0.00024	-0.00600	-0.00218
shape	-0.00759	-0.00327	-0.01045	-0.00780	-0.00789	-0.00502	-0.01726	-0.01651
dis-in	-0.00031	-0.00019	-0.00032	-0.00025	-0.00029	-0.00020	-0.00041	-0.00035
quad-dis	0.00302	0.00255	0.00293	0.00262	0.00274	0.00227	0.00339	0.00301
shape-in	0.00027	0.00083	0.00041	0.00092	0.00037	0.00099	0.00090	0.00180
shape-dis	0.00570	0.00537	0.00857	0.00833	0.00793	0.00742	0.01853	0.01802
quad-in		-0.00019		-0.00012		-0.00016		-0.00013
quad-shape		0.00752		0.00601		0.00803		0.00955
Total	-0.18160	0.04133	0.15012	0.36498	0.83266	1.04826	1.40867	1.71184

TABLE III. Quantum corrections to the configurational internal energy, entropy, and pressure for fluid H<sub>2</sub>.

T	$\rho$	$100 \frac{U-U^c}{U^c}$	$100 \frac{S-S^c}{S^c}$	$100 \frac{P-P^c}{P^c}$
(K)	(mol l <sup>-1</sup> )			
120	9.468	-16.88	0.90	5.71
	14.973	-15.95	1.50	9.43
	30.322	-15.91	4.08	21.52
100	9.468	-25.29	1.51	8.55
	14.973	-23.37	2.47	14.45
	30.322	-22.10	6.70	33.57
80	9.468	-42.32	2.86	15.35
	14.973	-38.52	4.73	25.89
	30.322	-33.90	12.46	64.29

TABLE IV. Compressibility and entropy of fluid H<sub>2</sub>.

T	$\rho$	$\beta P/\rho$			$S/Nk$		
		With $u_{in}$	Without $u_{in}$	Experimental	With $u_{in}$	Without $u_{in}$	Experimental
120	9.468	1.0743	1.0776	1.0726	7.9689	7.9673	7.996
100	11.540	1.0665	1.0708	1.0560	7.2240	7.2213	7.400
80	14.973	1.0484	1.0545	1.0174	6.3342	6.3291	6.642
60	21.619	1.0430	1.0523	0.9395	5.3521	5.3403	5.557
60	16.342	0.9940	1.0011	0.9361			

we find that the results calculated in the presence of the induced interaction  $u_{in}$  are better. Further, the agreement is good at high temperature, which decreases with the decrease of temperature. For example, in case of pressure, the percentage of error is less than 1% for  $T \geq 100$  K, whereas in the case of the entropy the percentage of error is 0.34% at  $T=120$  K,  $\rho=9.468$  mol  $l^{-1}$  and 2.38% at  $T=100$  K,  $\rho=11.540$  mol  $l^{-1}$ . However, for lower temperatures, the percentage of error is large. One should

consider the higher-order quantum corrections to get better results at lower temperatures.

#### ACKNOWLEDGMENTS

One of us (A.K.S.) gratefully acknowledges the financial support of University Grants Commission (UGC) New Delhi, India.

#### APPENDIX A

Expressions for terms appearing in Eq. (15) are given by

$$[f_{tr}^I(\text{LJ})]^* = \frac{1}{4\pi^2} [\rho^* / (T^*)^2] [22 \langle (r^*)^{-14} \rangle_2 - 5 \langle (r^*)^{-8} \rangle_2], \quad (\text{A1})$$

$$[f_{tr}^I(\text{in})]^* = -\frac{3}{4\pi^2} [\rho^* \alpha^* (\theta^*)^2 / (T^*)^2] \left[ \frac{7}{3} \langle (r^*)^{-10} \rangle_2 - \frac{1}{T^*} (22 \langle (r^*)^{-22} \rangle_2 - 5 \langle (r^*)^{-16} \rangle_2) \right], \quad (\text{A2})$$

$$[f_{tr}^I(\text{quad})]^* = -\frac{7}{12\pi^2} [\rho^* (\theta^*)^4 / (T^*)^3] \langle (r^*)^{-12} \rangle_2, \quad (\text{A3})$$

$$[f_{tr}^I(\text{anis-dis})]^* = -\frac{1}{\pi^2} [\rho^* / (T^*)^3] [K^2 (2 + \frac{19}{5} K^2) \langle (r^*)^{-14} \rangle_2 + 2\rho^* K^2 \langle [(r_{12}^*)^{-8} (r_{13}^*)^{-6}] P_2 \cos(\theta_1) \rangle_3], \quad (\text{A4})$$

$$[f_{tr}^I(\text{shape})]^* = -\frac{176}{5\pi^2} [\rho^* D^2 / (T^*)^3] \langle (r^*)^{-26} \rangle_2, \quad (\text{A5})$$

$$[f_{tr}^I(\text{dis-in})]^* = -\frac{86}{35\pi^2} [\rho^* \alpha^* (\theta^*)^2 K / (T^*)^3] \langle (r^*)^{-16} \rangle_2, \quad (\text{A6})$$

$$[f_{tr}^I(\text{quad-dis})]^* = \frac{3}{\pi^2} [\rho^* K^2 (\theta^*)^2 / (T^*)^3] \langle (r^*)^{-13} \rangle_2, \quad (\text{A7})$$

$$[f_{tr}^I(\text{shape-in})]^* = \frac{376}{35\pi^2} [\rho^* \alpha^* (\theta^*)^2 D / (T^*)^3] \langle (r^*)^{-22} \rangle_2, \quad (\text{A8})$$

$$[f_{tr}^I(\text{shape-dis})]^* = \frac{108}{5\pi^2} [\rho^* K D / (T^*)^3] \langle (r^*)^{-20} \rangle_2. \quad (\text{A9})$$

#### APPENDIX B

Expressions for terms appearing in Eq. (16) are given by

$$[f_{rot}^I(\text{quad})]^* = -\frac{1}{192\pi^2} [\rho^* / (T^*)^2] \left[ \frac{1}{3} (\theta^*)^2 \langle (r^*)^{-5} \rangle_2 - \frac{848}{27} [(\theta^*)^4 / (T^*)] \langle (r^*)^{-10} \rangle_2 \right] \quad (\text{B1})$$

$$[f_{rot}^I(\text{in})]^* = \frac{3}{40\pi^2} [\rho^* (\alpha^*)^2 (\theta^*)^4 / (T^*)^3] \langle (r^*)^{-16} \rangle_2, \quad (\text{B2})$$

$$[f_{rot}^I(\text{anis-dis})]^* = \frac{1}{5\pi^2} [\rho^* / (T^*)^3] K^2 (1 + \frac{19}{5} K^2) \langle (r^*)^{-12} \rangle_2, \quad (\text{B3})$$

$$[f_{rot}^I(\text{shape})]^* = \frac{4}{5\pi^2} [\rho^* D^2 / (T^*)^3] \langle (r^*)^{-24} \rangle_2, \quad (\text{B4})$$

$$[f_{rot}^I(\text{quad-in})]^* = -\frac{183}{6720\pi^2} [\rho^* \alpha^* (\theta^*)^4 / (T^*)^3] \langle (r^*)^{-13} \rangle_2, \quad (\text{B5})$$

$$[f_{rot}^I(\text{quad-dis})]^* = \frac{7}{180\pi^2} [\rho^* (\theta^*)^2 / (T^*)^3] K (2 - \frac{93}{5} K) \langle (r^*)^{-11} \rangle_2, \quad (\text{B6})$$

$$[f_{rot}^I(\text{quad-shape})]^* = \frac{143}{720\pi^2} [\rho^* (\theta^*)^2 D / (T^*)^3] \langle (r^*)^{-17} \rangle_2, \quad (\text{B7})$$

$$[f_{rot}^I(\text{dis-in})]^* = \frac{3}{35\pi^2} [\rho^* \alpha^* (\theta^*)^2 K / (T^*)^3] \langle (r^*)^{-14} \rangle_2, \quad (\text{B8})$$

$$[f_{\text{rot}}^I(\text{shape-in})]^* = \frac{12}{35\pi^2} [\rho^* \alpha^* (\theta^*)^2 D / (T^*)^3] \langle (r^*)^{-20} \rangle_2, \quad (\text{B9})$$

$$[f_{\text{rot}}^I(\text{shape-dis})]^* = -\frac{2}{5\pi^2} [\rho^* DK / (T^*)^3] \langle (r^*)^{-18} \rangle_2. \quad (\text{B10})$$

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<sup>1</sup>A. K. Singh and S. K. Sinha, *Phys. Rev. A* **30**, 1078 (1984).

<sup>2</sup>C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Oxford University Press, London, 1984), Vol. 1.

<sup>3</sup>P. Clancy and K. E. Gubbins, *Mol. Phys.* **44**, 581 (1981).

<sup>4</sup>D. A. Young and M. Ross, *J. Chem. Phys.* **74**, 6950 (1981); D. A. Young, *Phys. Rev. A* **23**, 1498 (1981).

<sup>5</sup>J. G. Powles and G. Rickayzen, *Mol. Phys.* **38**, 1875 (1979).

<sup>6</sup>K. P. Shukla, S. Singh, and Y. Singh, *J. Chem. Phys.* **70**, 3086 (1979).

<sup>7</sup>M. S. Ananth, Ph.D. dissertation, University of Florida, 1972.

<sup>8</sup>J. Hilsenrath, H. J. Hoge, C. W. Beckett, J. F. Masi, W. S. Benedict, R. L. Nuttall, L. Fasso, Y. S. Touloukian, and H. W. Woolley, *Tables of Thermodynamic and Transport Properties* (Pergamon, New York, 1960).