Statistical Mechanical Theory of Rod-Like Molecular Fluids with Kihara-Type Interactions. II. Thermodynamic Properties

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Statistical Mechanical Theory of Rod-Like Molecular Fluids with Kihara-Type Interactions

II. Thermodynamic Properties

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Expressions for thermodynamic properties as functionals of a pair distribution function depending only on the shortest distance between molecular cores are presented. Values of internal energy, entropy, enthalpy and pressure, by two ways, were computed for a linear core and for a spherical core of CO_2 molecule.

Pair distribution function for linear core is taken from a new approximation derived by the authors in a previous paper, to solve Percus–Yevick equation for linear molecules. Pair distribution function for spherical core is calculated from the Percus–Yevick equation by standard methods. The comparison with experimental results shows non-spherical theory improves considerably the agreement.

A brief discussion about the scope of the approximations made in the derivation of non-spherical theory is presented.

I INTRODUCTION

In a previous paper,[1] hereinafter referred to as I, the authors have written down a theory for the pair distribution function of a fluid of linear molecules. It was assumed there that the molecules can be well represented by a hard core linear segment with interactions depending only on the shortest distance, ρ, between cores. In order to get the theory manageable, two basic hypotheses

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have been done, i.e., the molecular distribution function also depends only on ρ, and the direct correlation function can be approximated by some average value, $\langle c \rangle$, conveniently defined.

The main objects of this paper are, firstly, to extend the theory to thermodynamic quantities, secondly, to examine its consistence on these properties and, thirdly, to get insight on the hypothesis just mentioned. Equations for thermodynamic quantities are developed in Section 2 while Section 3 is devoted to apply the theory to carbon dioxide.

As we will justify later, we think the way to compute $\langle c \rangle$ overestimates the softness of potential, specially for distances around σ. On the other hand, it seems well established[2] Kihara potential overestimates the steepness of potential at lower distances than σ and probably some cancellation of errors occurs. Besides, the high quadrupolar moment of CO_2 introduces a long-range interaction which can be probably well described in our approximation. The choice of CO_2 is important because, as we will show in Section 3, the resolution of Percus–Yevick (PY) equation for a spherical potential takes to very bad results for thermodynamic properties and our approximation improves considerably these results.

Finally, the results are commented on in Section 4.

II THEORETICAL EQUATIONS FOR THERMODYNAMIC PROPERTIES

The system to be considered is a fluid of N non-spherical molecules, whose total potential energy, U, is assumed pair-additive:

$$U = \sum_{i,j} u(q_i, q_j) \tag{1}$$

Here $u(q_1, q_2)$ is the intermolecular potential energy and $q = \{R, \Omega\}$ stands for the position (R) and orientation (Ω) molecular coordinates. The configurational integral for this system is

$$Q = \int \cdots \int \exp\left(-\frac{U}{kT}\right) dq_1 \cdots dq_N \tag{2}$$

and its molecular pair distribution function is given by

$$g(q_1, q_2) = \frac{64\pi^4 N(N-1)}{n^2 Q} \int \cdots \int \exp\left(-\frac{U}{kT}\right) dq_3 \cdots dq_N \tag{3}$$

with $n = N/V$, and the normalization condition

$$\int d\Omega = 8\pi^2 \tag{4}$$

for the rotational coordinates Ω.

On the other hand, for a system with angle-dependent potential energy, the internal energy, E, and pressure, p, are given, in terms of the distribution function $g(q_1, q_2)$, by the well-known general expressions[3]

$$E = 3NkT^2 \left(\frac{\partial \ln \Lambda}{\partial T}\right)_{V,N} + \frac{n^2}{128\pi^2} \iint u(q_1, q_2) g(q_1, q_2) \, dq_1 \, dq_2 \qquad (5)$$

$$\frac{pV}{NkT} = 1 - \frac{n^2}{384\pi^4 VkT} \iint r_{12} \frac{u(q_1, q_2)}{r_{12}} g(q_1, q_2) \, dq_1 \, dq_2 \qquad (6)$$

$$r_{12} = |R_1 - R_2| \qquad (7)$$

Under the assumption outlined in paper I, namely, the pair distribution function is a function of the shortest distance, ρ, between molecular cores, only, the above equations are simplified to

$$\frac{E}{NkT} = 3T \left(\frac{\partial \ln \Lambda}{\partial T}\right)_{V,N} + \frac{n}{2kT} \int_0^\infty S_{c+\rho+c} u(\rho) g(\rho) \, d\rho \qquad (8)$$

$$\frac{pV}{NkT} = 1 - \frac{n}{2kT} \int_0^\infty V_{c+\rho+c} \frac{du(\rho)}{d\rho} g(\rho) \, d\rho \qquad (9)$$

with

$$S_{c+\rho+c} = 2S_c + 4\pi(2R_c^2 + 4\pi R_c \rho + \rho^2) \qquad (10)$$

$$V_{c+\rho+c} = 2V_c + 2R_c S_c + 2S_c \rho + 4\pi\left(2R_c^2 \rho + 2R_c \rho^2 + \frac{\rho^3}{3}\right) \qquad (11)$$

Here $g(\rho)$ is the pair distribution function introduced in I; R_c is 4π times the integral of the mean curvature of molecular core, and S_c and V_c its surface and volume, respectively.

In going from Eqs. (5) and (6) to Eqs. (8) and (9), the following expressions were used[4]

$$dq_j = dV_j \, d\Omega_j = \mathbf{u}_{ij} \cdot \left(\frac{\partial \mathbf{r}_{ij}}{\partial \theta_j} \times \frac{\partial \mathbf{r}_{ij}}{\partial \phi_j}\right) \sin \xi_j \, d\theta_j \, d\phi_j \, d\xi_j \, d\psi_j d\zeta_j \, d\rho_{ij} \qquad (12)$$

$$\int \mathbf{u}_{ij} \cdot \left(\frac{\partial \mathbf{r}_{ij}}{\partial \theta_j} \times \frac{\partial \mathbf{r}_{ij}}{\partial \phi_j}\right) \sin \xi_j \, d\theta_j \, d\phi_j \, d\xi_j \, d\psi_j \, d\zeta_j = 8\pi^2 S_c \qquad (13)$$

$$\int \mathbf{r}_{ij} \cdot \left(\frac{\partial \mathbf{r}_{ij}}{\partial \theta_j} \times \frac{\partial \mathbf{r}_{ij}}{\partial \phi_j}\right) d\theta_i \, d\phi_j = 3V_{c+\rho_{ij}+c} \qquad (14)$$

$$\mathbf{r}_{ij} \cdot \frac{\partial u(\rho_{ij})}{\partial r_{ij}} = \left(\frac{du(\rho_{ij})}{d\rho_{ij}}\right) \mathbf{r}_{ij} \cdot \mathbf{u}_{ij} \qquad (15)$$

where all undefined symbols have the same meaning as in I.

By using standard methods[5] one can obtain the chemical potential, too, as

$$\frac{\mu}{kT} = \ln\left(\frac{n\Lambda^3}{8\pi^2}\right) + \frac{n}{kT} \int_0^1\int_0^\infty S_{c+p+c}\, u(\rho, \xi)g(\rho, \xi)\, d\rho\, d\xi \qquad (16)$$

Other thermodynamic properties can be computed from any of these quantities through suitable thermodynamic equations.[6]

III RESULTS FOR CO_2

The theory set up in the last section is applied here to obtain thermodynamic properties of CO_2. Kihara potential

$$u(\rho) = 4\varepsilon\left(\left(\frac{\sigma}{\rho}\right)^{1/2} - \left(\frac{\sigma}{\rho}\right)^6\right) \qquad (17)$$

with a rectilinear segment core of length $L = 2.3$ A, $\sigma = 2.940$ A and $\varepsilon/k = 316$ K, is used for molecular interactions.[7] The pair distribution function, $g(\rho)$, for this potential was obtained from the integral equation (Eq. 18) of I which was solved by the numerical methods described in that paper.

Figure 1 shows the pressure values obtained from the virial equation (Eq. 9) at gaseous densities and subcritical temperatures. Experimental data[8] are also included for comparison sake. Agreement between theory and experiment is excellent up to densities on the experimental saturation curve. However, at higher densities, calculations show that the pressure from Eq. 9 continuously decreases on increasing density even at densities outside the physical region. Later, in Section 4, we will attempt a plausible explanation for this anomalous behaviour. For temperatures above the critical experimental isotherm (Figure 2), the non-spherical theory considerably improve the results from the spherical core Kihara potential. The results for the spherical case, included in Figure 2, were obtained by the authors following Lee and Hulburt[9] and using the potential parameters $\sigma = 3.056$ A, $\varepsilon/k = 311$ K and $r_{core} = 0.523$ A.[10]

On Figure 3 computed values and experimental data[8] for the configurational contribution to internal energy are plotted against the density at 280 K. Agreement is again good even though less satisfactory than virial pressure was. However, this goodness of the energy remains over a large range of temperature and density than that of the pressure computed from the virial equation. Thus, energy equation (Eq. 8) seems to be a useful alternative way to obtain thermodynamic properties, less sensible to errors in the range 0.85–0.95σ,[11] and will be used in the following to compute the other thermodynamic properties. Figure 4 includes also energy values for the Kihara
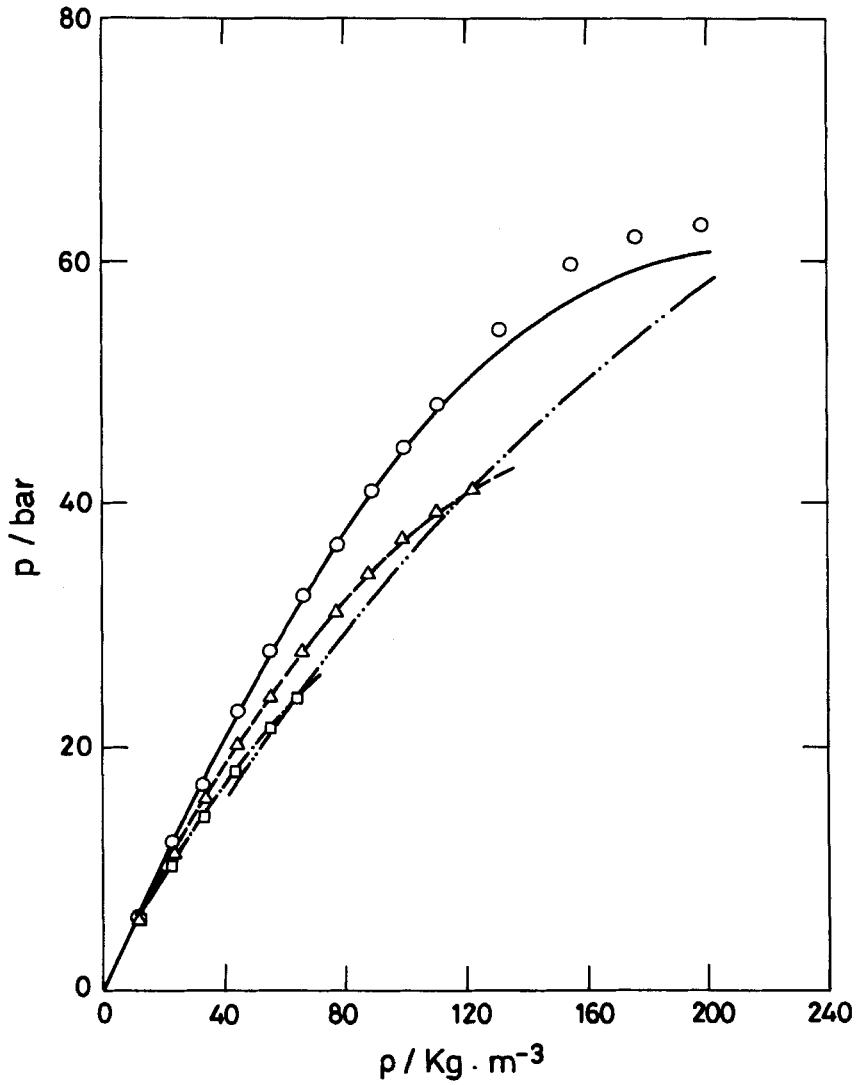
FIGURE 1   Pressure at subcritical temperatures. Temperatures are close to the experimental critical one (T_c = 304.21 K). Curves represent values from the virial equation (Eq. 9) and dots are experimental points[8] —··—··— is the experimental saturation curve and ○ ——— 310 K; △ — — — 280 K; □ —·—·— 260 K.
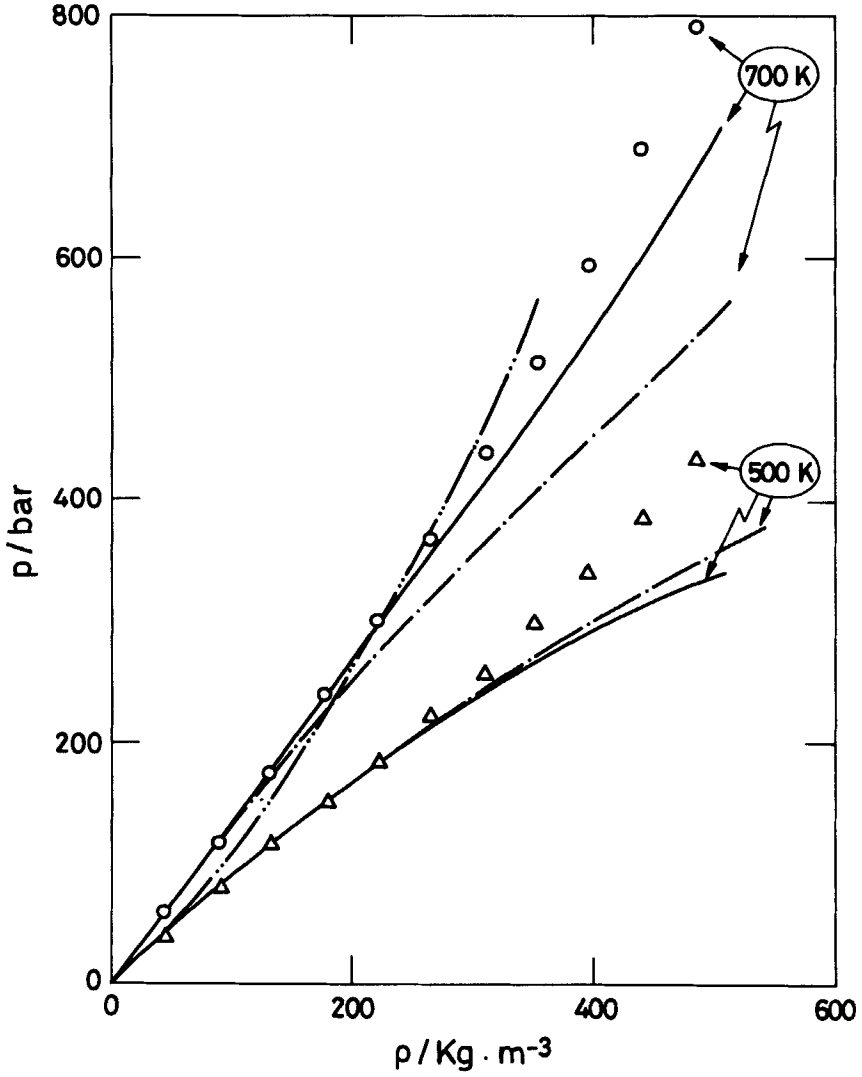
FIGURE 2   Pressure at high temperatures. Full lines are values from the virial equation
(Eq. 9), broken line values from the energy equation (Eq. 8), dotted line from the spherical model
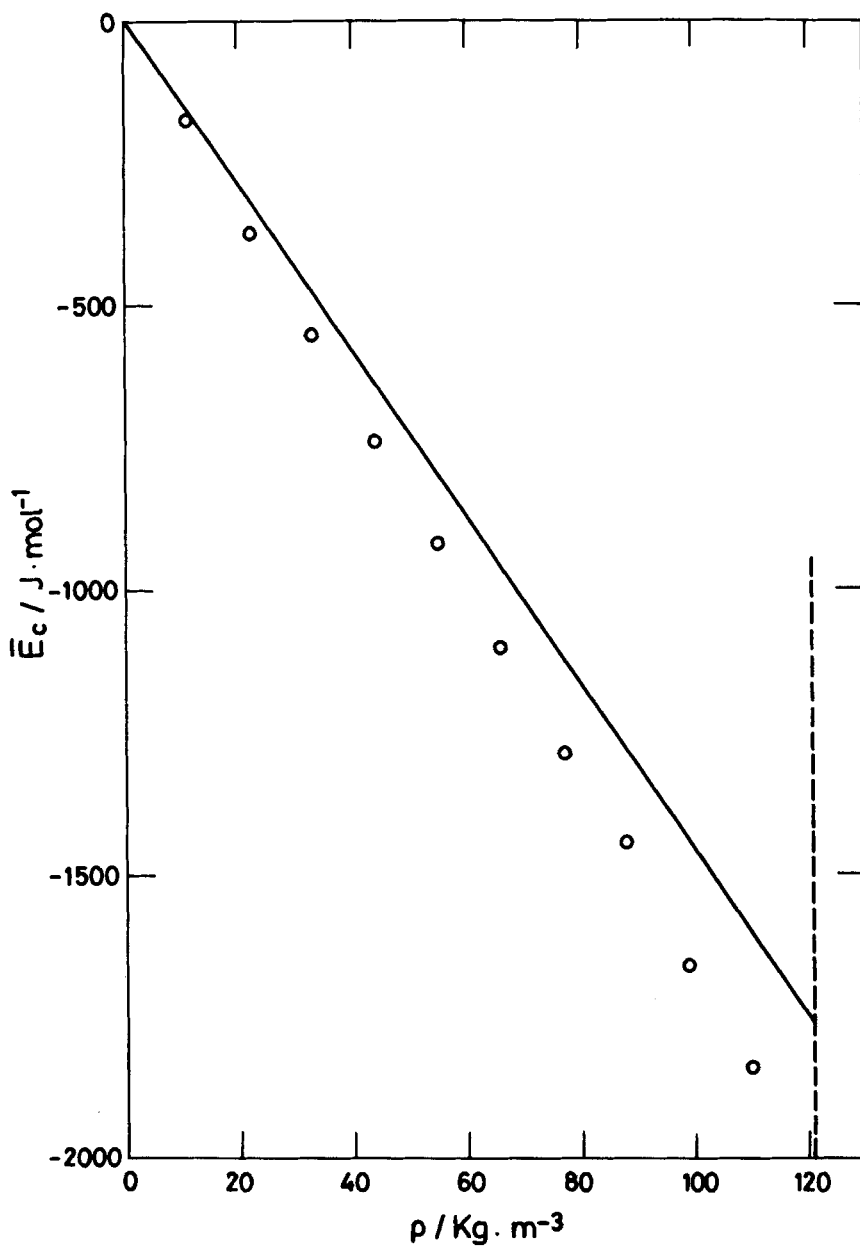(virial equation) and circles and triangles are experimental points.

FIGURE 3   Configurational energy at 280 K. Full line corresponds to theoretical values, circles are experimental points[8] and dashed line is the experimental saturation curve.
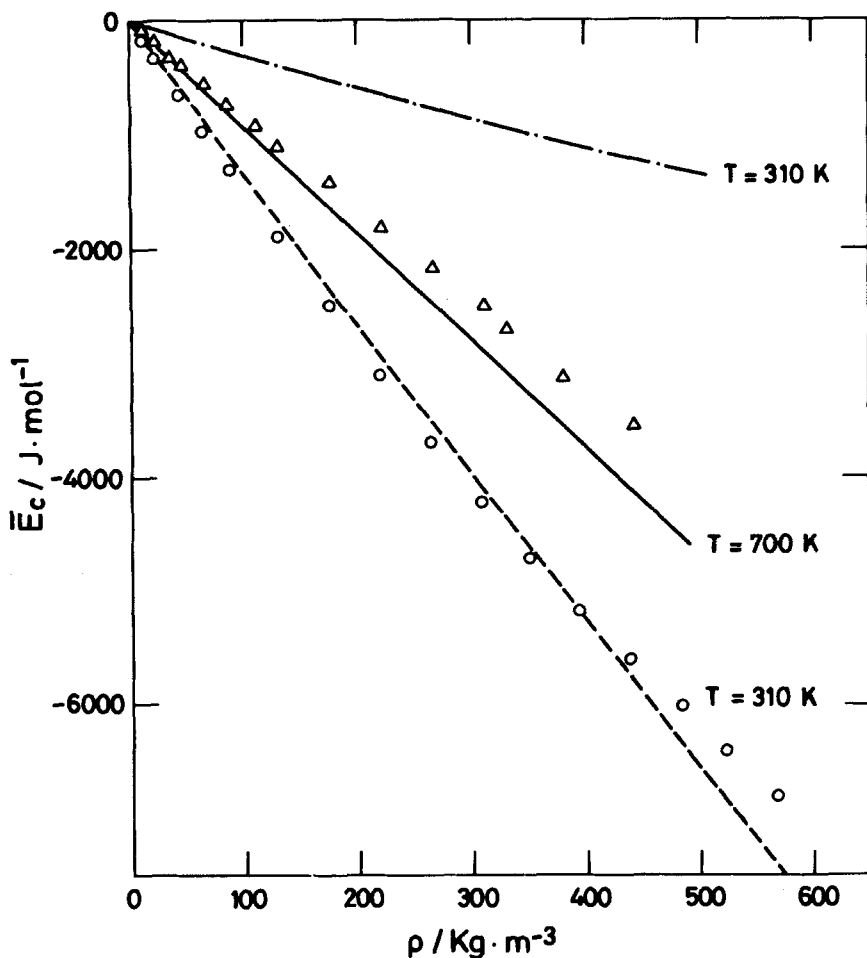
FIGURE 4   Configurational energy for spherical ($- \cdot - \cdot -$) and non-spherical ($- - - -$ and
———) models. Dots are experimental points[8] at 310 K (○) and 700 K (△).

potential with spherical core at 310 K. The improvement of results when one
goes from spherical models to non-spherical models is even more meaningful
here, where the spherical model results exhibit a large departure respect to
experimental data. On the other hand, it is seen that, in general, the non-
spherical model underestimates the configurational energy at high tempera-
tures and overestimates it at low temperatures. Nevertheless, deviations do
not exceed never 15 per cent. Since the configurational part represents not
more than 30 per cent about on the total internal energy, one can conclude
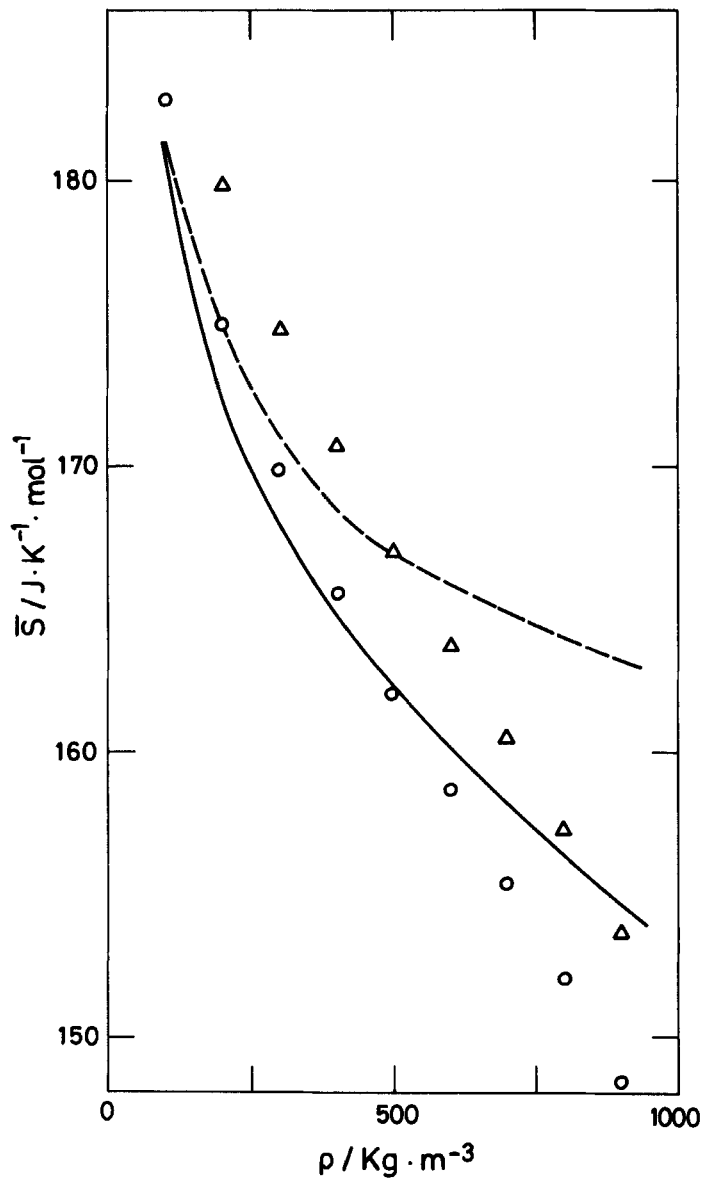that this last quantity is determined with errors of 4–5 per cent maximum.

FIGURE 5 Entropy vs. density. Lines are theoretical values and dots experimental points,[8] with ◯ ———— 350 K and △ — — — — — 400 K.
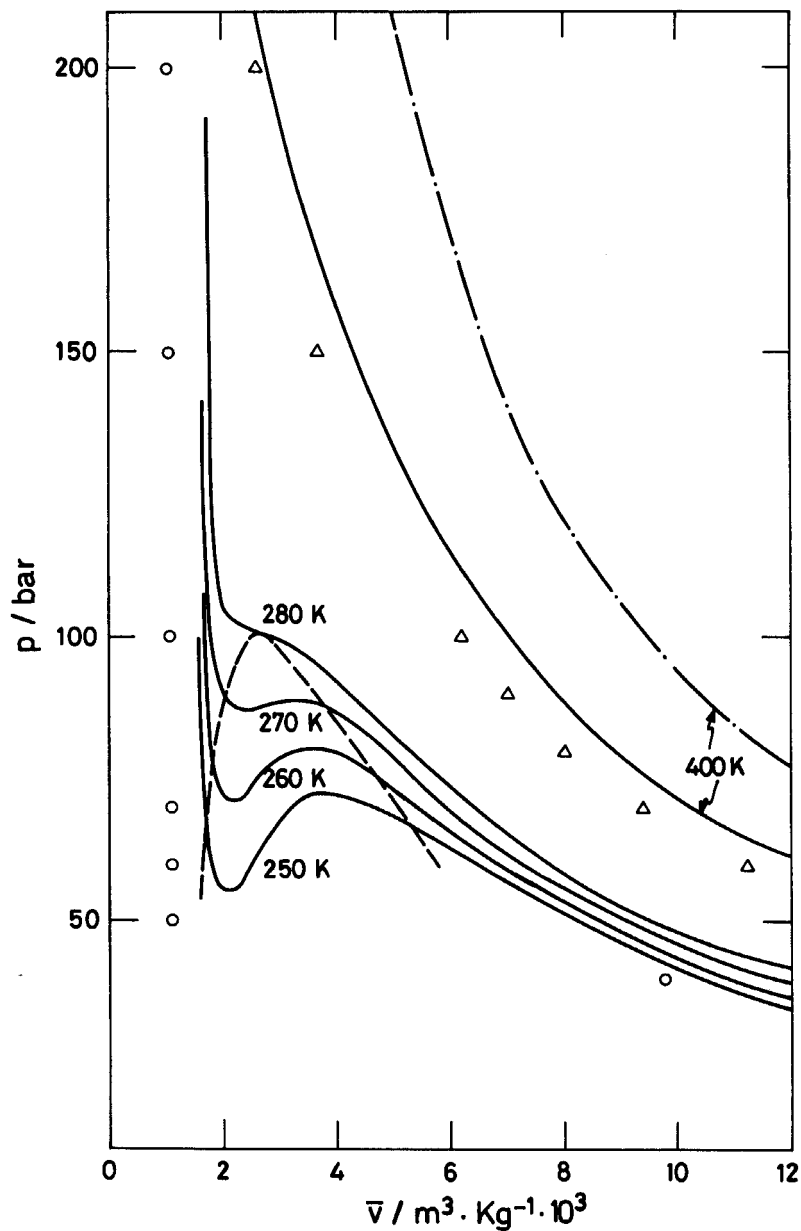
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FIGURE 6   Pressure from the energy equation (Eq. 9): —·—·— results for the spherical model; ———— results for the non-spherical model; — — — — theoretical curve of saturation. Dots are experimental values at 260 K (○) and 400 K (△).
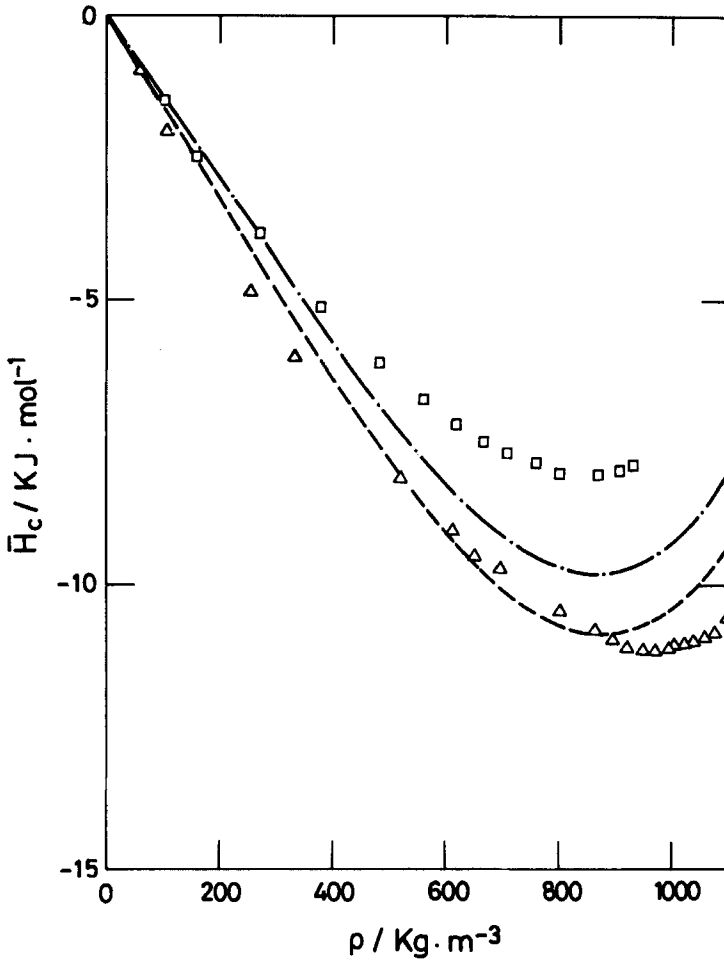
FIGURE 7   Configurational enthalpy vs. density: $\triangle$ — — — — 310 K and $\square$ — · — · — 400 K.

Entropy, enthalpy and, even, pressure were computed from theoretical energy data from Eq. 8. To obtain entropy a numerical integration of the energy data with respect to $1/T$ was performed. Here the integration constant was fixed by putting it equal to experimental entropy at 310 K. Entropy could also be evaluated starting from Eq. 15 but the required computational time makes this procedure almost prohibitive. The calculated entropy at 350 and 400 K is plotted in Figure 5 together with experimental points.[8] It is seen the theory yields to a system with a higher order than the actual one at low densities and lower order at higher densities. These results seem

to be consistent with the too low values of pressure at high densities if we suppose that the approximations in the Eq. (18) of paper I underestimates the repulsive part of potential. Pressure from energy equation is given in Figures 2 and 6. In contrast to virial equation, results exhibit a right qualitative behavior over all the density range. Indeed, there exist a temperature, T_c, under which the pressure increases with increasing density for densities inside the experimental liquid region. Figure 6 also includes pressure values for Kihara's spherical model at 400 K. Looking at this figure, it is clear the non-spherical model improves once again the results in a very important manner.

Classical van der Waals rule of equal areas was used to compute liquid-vapor coexistence volumes and then obtain the saturation curve (Figure 6) and critical point. The critical constants were found to be $T_c = 280 \pm 1$ K, $\rho_c = 0.40 \pm 0.01$ g·cm^{-3}, $p_c = 99.2 \pm 0.1$ bar and $z_c = 0.47 \pm 0.01$. Since the experimental values are $T_c = 304.21$ K, $\rho_c = 0.466$ g·cm^{-3}, $p_c = 73.82$ bar and $z_c = 0.276$, it can be stated that the agreement between theory and experiment is satisfactory at the critical point, except for the compressibility factor. Besides, the slope of the theoretical saturation curve (Figure 6) along its two branches is lower than that of the experimental one.[8] It yields to important deviations from the experimental data of coexistence densities, in spite of which they seem to be the best results, in our knowledge, reached up to now by this type of theories without *ad hoc* adjustable parameters.

Theoretical and experimental[8] configurational enthalpy values are compared on Figure 7. The agreement here is of the same order as in the energy case but perhaps less satisfactory.

IV   DISCUSSION AND CONCLUSIONS

The above results obtained for the set of thermodynamic properties can be qualified as good, specially if one thinks that CO_2 is a very difficult molecule to describe. However, there are several points to consider:

a) at experimental liquid densities, pressure from virial equation decreases systematically and does not increase again for densities close to experimental liquid one;

b) at liquid densities the theoretical model shows a lower order than that of the actual system; the opposite is true at low densities, and

c) at high temperatures, pressure from both virial and energy equations is everywhere lower than the experimental one. This behavior is surprising because it seems well established that Kihara potential overrates the repulsive forces and yields too high pressures.

It is our belief that the main source of such difficulties could come from neglecting the most repulsive contributions to $\langle c \rangle$ in Eq. (18) of I, at short distances. Surely, this fact produces a too broad first maximum in $g(\rho)$ and therefore yields too low values for z and p. In some sense, the underestimation of the repulsive character of molecular interactions, brought into the theory through those assumptions on the direct correlation function at small molecular separations, balance the overrating which the Kihara interaction model implies. If we are right, such compensating mechanism would explain the satisfactory results obtained from a theory which apparently rests on very drastic approximations. On the other hand, since the liquid structure is basically governed by the repulsive forces the underestimating effects of the theory could also explain the excess in the theoretical entropy at high densities.

In conclusion, the theory derived in I seems to represent a positive step in dealing with polyatomic fluids of linear molecules, specially to calculate its thermodynamic properties. On the other hand, it can be probably improved by further approximations to direct the correlation function.[1]

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