Perturbation theory of non-spherical molecule fluids

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Abstract : Perturbation theory for non-spherical molecule fluids is considered, in which the GOCE poetntial is taken as a reference and the electrostatic interactions as a perturbation. Theoretical expressions are given for perturbation terms. The properties of the reference GOCE fluid are determined using the peturbation theory of Singh *et al* [12]. The numerical calculations are made for the thermodynamic properties such as internal energy, entropy and pressure for N_2 and CO_2 using the Gaussian parameters and comparisons are made with the experimental data. The agreement is found to be good

1. Introduction

In recent years, theoretical and experimental efforts have been made to understand the structural and thermodynamic properties of polar non-spherical molecular fluids [1–5]. Several potential models such as multicentre (atom-atom) or Kihara generalised pair potential have been proposed for molecular fluids of non-spherical molecules [1]. The atom-atom potential model is convenient for use for small molecule like N_2 but inconvenient for larger molecules (*e.g.* C_6H_6). Further the dependence on molecular orientation in the atom-atom model is implicit, so that it is difficult to use in analytic perturbation calculation. The Gaussian overlap (GO) model of Berne and Pechukas [6] is of special interest because it proved to be solvable one. The GO madel may be viewed as an interaction between molecules whose repulsive cases are basically ellipsoids of revolutions. This model has certain deficiencies as pointed out by Gray and Berne [7]. Even then this model is sufficiently realistic [8] and may be employed to fluids of non-spherical molecules. Particularly, it may not lead any serious error in estimating the thermodynamic properties of molecular fluids, where we perform integration over orientations [9].

Considerable progress has been made in the study of polar non-spherical fluids. The approach for studying the properties of these systems is the extended version of the Barker-Pople-Gubbin-Gray (BPGG) perturbation theory [1] in which the Kihara potential serves as reference and the effect of the electrostatic interactions is considered as a perturbation. The reference distribution function (of convex molecules) in the perturbation terms is approximated by that of the GO fluid [3,4]. Employing the decoupling approximation [10] for the Gaussian distribution function, the perturbation integrals become simpler for evaluation.

In this paper, we extend the perturbation theory, originally developed by Boublik [2,4], for non-spherical molecular fluid, where the GO potential is taken as a reference and the electrostatic as well as the anistropy of short range overlap interactions as a perturbation. The perturbation terms in this case are directly expressed in terms of the distribution function of the GO fluid. To determine the thermodynamic properties of the GO fluid,.we employ the Weeks-Chandler-Anderson (WCA) [11] type perturbation theory developed by Singh *et al* [12].

The paper is organised as follows. In Section 2, the theory for thermodynamic properties of the non-spherical molecular fluid is discussed. The perturbation theory for the GO fluid is described in Section 3. The results for N_2 and CO_2 are discussed in Section 4. The paper ends with the concluding remarks in Section 5.

2. Theory

We consider non-spherical molecule fluid, whose molecules interact *via* pair-potential, given by a sum of two terms.

$$u(r, \omega_1 \omega_2) = u_{GO}(r, \omega_1 \omega_2) + V(r, \omega_1 \omega_2), \qquad (1)$$

where u_{GO} is the Gaussian overlap potential model of Berne and Pechukas [6]

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$$u_{GO}(r,\omega_1\omega_2) = 4\varepsilon(\omega_1\omega_2)[(\sigma(\omega_1\omega_2)/r)^{12}$$
$$-(\sigma(\omega_1\omega_2)/r)^6],\qquad(2)$$

where

$$\sigma(\omega_1\omega_2)/\sigma_0 = [1-\chi(\cos^2\theta_1+\cos^2\theta_2-$$

$$2\chi\cos\theta_1\cos\theta_2\cos\theta_{12})/(1-\chi^2\cos^2\theta_{12})]^{-1/2}\qquad(3)$$

and

$$\varepsilon(\omega_1\omega_2)/\varepsilon_0 = [1-\chi^2\cos^2\theta_{12})]^{-1/2}.\qquad(4)$$

Here, $r = |r_1 - r_2|$ is the centre to centre distance, ω_i represents the orientation cordinates (θ_i, ϕ_i) and θ_1, θ_2 and θ_{12} are the Euler angles. The constants ε_0 and σ_0 have the dimensions of energy and length, respectively and χ the anistropy parameter defined as

$$\chi = (K^2-1)/(K^2+1).\qquad(5)$$

Thus, the GO model is a three parameter one $\{\varepsilon_0, \sigma_0$ and $\chi\}$, where χ determines the shape, prolate or oblate of the molecules, K is the length-to-width ratio $(2a/2b)$ of the molecules such that $K > 1$ for prolate and $K < 1$ for oblate molecules. For spheres $K = 1$, eq. (2) simply reduces to the Lennard-Jones (LJ) (12-6) potential for spherical molecules. In the special case of the Gaussian overlap with constant energy (GOCE) model [9], $\varepsilon(\omega_1\omega_2) = \varepsilon_0$. Kabadi and Steele [9] have shown that use of ε_0 instead of $\varepsilon(\omega_1\omega_2)$ does not change the thermodynamic properties much. In the present calculation, we use the GOCE model. For the second term in eq. (1), we take

$$V = u_{perm} + U_{in},\qquad(6)$$

where u_{perm} is the interaction between multipole moments of the molecules and u_{in} is the interaction of the induced multipole moment in one molecule with the permanent multiple moments in the other. They are expressed as [1,13]

$$u_{perm} = (\mu^2/r^3)\Phi_{\mu\mu}(\omega_1\omega_2)+(3/2)(\mu Q/r^4)\Phi_{\mu Q}(\omega_1\omega_2)$$

$$+(3/4)(Q^2/r^5)\Phi_{QQ}(\omega_1\omega_2)\qquad(7a)$$

and $\quad u_{in} = -(1/2)(\alpha\mu^2/r^6)\Phi_{\alpha\mu}(\omega_1\omega_2) -$

$$(9/8)(\alpha Q^2/r^8)\Phi_{\alpha Q}(\omega_1\omega_2),\qquad(7b)$$

where

$$\Phi_{\mu\mu}(\omega_1\omega_2) = \sin\theta_1\sin\theta_2\cos\phi-2\cos\theta_1\cos\theta_2.\qquad(8a)$$

$$\Phi_{\mu Q}(\omega_1\omega_2) = \cos\theta_1(3\cos^2\theta_2-1) -$$

$$2\sin\theta_1\sin\theta_2\cos\theta_2\cos\phi,\qquad(8b)$$

$$\Phi_{QQ}(\omega_1\omega_2) = 1-5(\cos^2\theta_1+\cos^2\theta_2) -$$

$$15\cos^2\theta_1\cos^2\theta_2+2(\sin\theta_1\sin\theta_2\cos\phi -$$

$$4\cos\theta_1\cos\theta_2)^2,\qquad(8c)$$

$$\Phi_{\alpha\mu}(\omega_1\omega_2) = 2+3\cos^2\theta_1+3\cos^2\theta_2,\qquad(8d)$$

$$\Phi_{\alpha Q}(\omega_1\omega_2) = \sin^4\theta_1+\sin^4\theta_2+4\cos^4\theta_1+4\cos^4\theta_2.\qquad(8c)$$

Here, θ_1, θ_2 and $\phi = \phi_1 - \phi_2$ are the Euler angles, μ and Q are, respectively, the dipole and quadrupole moments and α the average polarizability. In the GO model, the attractive part of potential $-4\varepsilon(\omega_1\omega_2)[\sigma(\omega_1\omega_2)/r]^6$ is the dispersion potential and is given correctly, where as $4\varepsilon(\omega_1\omega_2)$ $|\sigma(\omega_1\omega_2)/r|^{12}$ is the repulsive part of potential, which treats the short range shape or overlap potential.

Using the perturbation theory, where u_{GO} is treated as the reference potential and V is the perturbation, the residual Helmholtz free energy of the molecular fluid can be written as

$$(A - A^*)/NkT = ((A_{GO} - A^*)/NkT)+(A_1/NkT)$$

$$+(A_2/NkT)+(A_3/NkT)+...,\qquad(9)$$

where A^* represents the Helmholtz free energy of an ideal gas and $A_{GO}-A^*$, the residual free energy of the reference GO fluid, and A_n is the n-th order perturbation correction term due to the perturbation potential V.

$$A_1/NkT = (1/2)\beta\rho\int <g_{GO}(r\omega_1\omega_2)V(r\omega_1\omega_2)>_{\omega_1\omega_2}dr_2.\qquad(10)$$

$$A_2/NkT = -(1/4)\beta^2\rho\int <g_{GO}(r\omega_1\omega_2)$$

$$[V(r\omega_1\omega_2)]^2>_{\omega_1\omega_2}dr_2\qquad(11)$$

and

$$A_3/NkT = (A_{32}/NkT)+(A_{33}/NkT)\qquad(12)$$

with

$$A_{32}/NkT = (1/12)\beta^3\rho\int <g_{GO}(r\omega_1\omega_2)$$

$$[V(r\omega_1\omega_2)]^3>_{\omega_1\omega_2}dr_2,\qquad(13)$$

$$A_{33}/NkT = (1/6)\beta^3\rho^2\int <g_{GO}(1,2,3)V(1,2)$$

$$V(1,3)V(2,3)>_{\omega_1\omega_2\omega_3}dr_2 dr_3.\qquad(14)$$

Here, $\beta = (kT)^{-1}$, g_{GO} $(r\ \omega_1\omega_2)$ and g_{GO} $(1,2,3)$ are pair and triple distribution function of the reference GO fluid and $\rho = N/V$ the number density (N is the number of molecule in a volume V). $<(...)>_{\omega_1\ ...\omega_1}$ represents an unweighted average over the molecular orientations $\omega_1, ..., \omega_1$ for the quantity within the angular bracket.

In order to evaluate the perturbation terms, we introduce the new variable r', defined by $r' = r/\sigma(\omega_1\omega_2)$, then the potential (eq. 2) transfers to be central Lennard-Jones (LJ) (12-6) potential. Consequently, the molecular pair distribution function (PDF) of the GO fluid becomes that of the LJ (12-6) fluid [3,7] i.e.

$$g_{GO}(r\omega_1\omega_2) \equiv g_{GO}(r/\sigma(\omega_1\omega_2)) = g_{LJ}(r').\qquad(15)$$

Substituting eq. (6) in eqs. (10) and (11) and using eq. (15),

the first and second order perturbation terms can be expressed as

$$A_1 / NkT = A_1(\text{in}) / NkT, \tag{16}$$

$$A_2 / NkT = A_2(\text{Perm}) / NkT, \tag{17}$$

where

$$A_1(\text{in}) / NkT = 2\pi(\rho^* / T^*)[(1/4)\alpha^* \mu^{*2} J_6^{\alpha\mu}(K)I_6$$

$$+(9/8)\alpha^* Q^{*2} J_8^{\alpha Q}(K)I_8], \tag{18}$$

$$A_2(\text{Perm}) / NkT = -\pi(\rho^* / T^{*2})[(\mu^{*2})^2 J_6^{\mu\mu}(K)I_6$$

$$+((3/2))\mu^* Q^*)^2 J_8^{\mu Q}(K)I_8 +(3/4Q^{*2})^2 J_{10}^{QQ}(K)I_{10}] \tag{19}$$

with

$$I_{nm}(\rho^*) = \int_v g_{IJ}(r^*)(\bar{r}^*)^{nm+2} dr^*, \tag{20}$$

$$J_{nm}^X(K) = < \Phi_x^n | \alpha(\omega_1\omega_2) / \sigma_0 |^{-nm+3} >_{\omega_1\omega_2}, \tag{21}$$

where n represents the order of perturbation term and m denotes the power of $(1/r)$ of the perturbation potential. In eqs. (18–19), we have used the following reduced quantities

$$\rho^* = \rho\sigma_0^3, \quad T^* = kT / \varepsilon_0, \quad \alpha^* = \alpha / \sigma_0^3,$$

$$\mu^{*2} = \mu^2 / \varepsilon_0\sigma_0^3, \quad Q^{*2} = Q^2 / \varepsilon_0\sigma_0^5. \tag{22}$$

In a similar way, the leading contribution to the third order perturbation term A_{32} may be written in the form

$$A_{32} / NkT = (1/3)\pi(\rho^* / T^{*3})[3\{(\mu^{*2})^2(3Q^{*2} / 4)J_{11}^{\mu2Q}(K)$$

$$+(\mu^{*2})(3\mu^*Q^* / 2)^2 J_{11}^{\mu\mu Q}(K)\}I_{11}$$

$$+3\left(\frac{3\mu^*Q^*}{2}\right)^2 (3Q^{*2} / 4)J_{13}^{\mu\mu Q}(K)I_{13}$$

$$+(3Q^{*2} / 4)^3 J_{15}^{Q3}(K)I_{15}], \tag{23}$$

where $J_{11}^{\mu2Q}$ and $J_{11}^{\mu\mu Q}$ are the coefficients, corresponding to $(\mu^2)^2(Q)^2$ and $(\mu^2)(\mu Q)^2$ respectively, while $J_{13}^{\mu QQ}$ and J_{15}^{Q3} are the coefficients, corresponding to $(\mu Q)^2(Q^2)$ and $(Q^2)^3$, respectively.

The values of the $J_n(K)$ integrals can be evaluated numerically for any value of K. Boublik [3] has given the functional equation to determine the integrals except $J_{15}Q3$. They are evaluated numberically for several values of K and reported in Table 1. The integral I_n at density $\rho^* = \rho^* K$ and temperature T^* can be evaluated following emperical equation of Ananth [14].

$$\ln I_n(\rho^*, T^*) = A_n\rho^{*2} \ln T^* + B_n\rho^{*2} + C_n\rho^* \ln T^*$$

$$+D_n\rho^* + E_n \ln T^* + F_n. \tag{24}$$

The coefficients $A_n - F_n$ for different values of n are reported by Gray and Gubbins [15].

Table 1. Values of J_n for different values of K

K	$J_{15}^{Q3}(K)$
1.00	4 17959
1.20	0 79097
1 30	0 55556
1.3419	0 51815
1 50	0 47915
1 55	0 47795
1.5637	0 47780
1 792	0 47208
1 80	0 47164
1 8836	0.46610
2.00	0 45620

Using the superposition approximation for g_{IJ} (1,2,3), the term A_{33} can be written as

$$A_{33} / NkT = (4\pi^2 / 3)(\rho^{*2} / T^{*3})[(\mu^{*2})^3 L_{\mu\mu\mu}$$

$$+3(\mu^{*2})^2(3Q^2 / 4)L_{\mu\mu Q} + 3(\mu^{*2})(3Q^{*2} / 4)^2 L_{\mu QQ}$$

$$+(3Q^{*2} / 4)^3 L_{QQQ}], \tag{25}$$

where

$$L = \int\int\int_\Delta M_{nmp}g_{IJ}(r_{12}^*)g_{IJ}(r_{23}^*)g_{IJ}(r_{31}^*)(r_{12}^*)^{n+1}$$

$$(r_{23}^*)^{-m+1}(r_{31}^*)^{-p+1}dr_{12}^*dr_{23}^*dr_{31}^*, \tag{26}$$

$$M_{nmp} = (4\pi)^{-3}\int\int\int \psi_n(\omega_1\omega_2)\psi_m(\omega_1\omega_3)$$

$$\psi_p(\omega_2\omega_3)d\omega_1d\omega_2d\omega_3 \tag{27}$$

and

$$\psi_n(\omega_i\omega_j) = \Phi(\omega_i\omega_j)[\sigma(\omega_i\omega_j) / \sigma_0]^{-n+2}. \tag{28}$$

Here, Δ denotes integration over r_{12}^*, r_{23}^* and r_{31}^* forming a triangle. The numerical integration of L in general is time consuming except for the μ–μ–μ and Q–Q–Q interactions. For these interactions L is given by Monte-Carlo (MC) interaction, which is fitted to formula [3]

$$L_{\mu\mu\mu} = 0.0236(1+2\eta+2\eta^2) / K^{1.063} \tag{29}$$

$$L_{QQQ} = 0.0155 \exp(4.3158\eta) / K^{2.65265} \tag{30}$$

where η is the packing fraction.

The total perturbation contribution to the Helmholtz free energy, ΔA is evaluated from the Pade' approximant [16]

$$\Delta A = A_1 + A_2(1 - A_3 / A_2)^{-1}. \tag{31}$$

The total residual free energy of the molecular fluid is determined as

$$(A - A^*) / NkT = (A_{GO} - A^*) / NkT + \Delta A / NkT. \tag{32}$$

The other thermodynamic properties follow from the respective derivatives of ΔA. Thus, the internal energy is obtained as

$$(U - U^*)/NkT = (U_{GO} - U^*)/NkT + \Delta U/NkT, \quad (33)$$

where

$$\Delta U/NkT = (1/T^*)(\delta(\Delta A/NkT)/\delta(1/T^*)). \quad (34)$$

Using eq. (31), one gets

$$\Delta U = U_1 + ((1 - 2A_3/A_2)U_2 + U_1)/(1 - A_3/A_2)^2. \quad (35)$$

Similarly the equation of state is

$$P/\rho kT = P_{GO}/\rho kT + \Delta P/\rho kT, \quad (36)$$

where

$$\Delta P/\rho kT = \rho^*(\delta(\Delta A/NkT)/\delta\rho^*) \quad (37)$$

which gives

$$\Delta P = P_1 + ((1 - 2A_3/A_2)P_2 + P_3)/(1 - A_3/A_2)^2. \quad (38)$$

Here, U_{GO} and P_{GO} are, respectively, the internal energy and pressure of the GO fluid.

3. Gaussian overlap fluid

In order to obtain the thermodynamic properties of the GO fluid we divide the GO potential u_{GO} into a reference part u_0 and perturbation part u_p, such that [12]

$$u_{GO}(r\omega_1\omega_2) = u_0(r\omega_1\omega_2) + u_p(r\omega_1\omega_2), \quad (39)$$

where

$$u_0(r\omega_1\omega_2) = u_{GO}(r\omega_1\omega_2) + \varepsilon(\omega_1\omega_2), \quad r < r_{min}(\omega_1\omega_2)$$
$$= 0, \quad\quad\quad\quad r > r_{min}(\omega_1\omega_2) \quad (40)$$

and

$$u_p(r\omega_1\omega_2) = -\varepsilon(\omega_1\omega_2), \quad r < r_{min}(\omega_1\omega_2)$$
$$= u_{GO}(r\omega_1\omega_2) \quad r > r_{min}(\omega_1\omega_2). \quad (41)$$

Here, $r_{min}(\omega_1\omega_2) = 2^{1/6}\sigma(\omega_1\omega_2)$. In the present calculation, we consider the GOCE model, where $\varepsilon(\omega_1\omega_2) \approx \varepsilon_0$.

Using this perturbation scheme, the Helmholtz free energy of the GOCE fluid is given by

$$A_{GO}/NkT = (A_0/NkT) + (1/2)\beta\rho \int dr$$
$$< g_0(r\omega_1\omega_2)u_p(r\omega_1\omega_2) >_{\omega_1\omega_2}. \quad (42)$$

where $g_0(r\omega_1\omega_2)$ is the PCF of the reference system.

The propetics of the reference system can be obtained by a blip function expansion about a suitably chosen hard Gaussian overlap (HGO) system. The HGO potential is

$$u_{HGO}(r\omega_1\omega_2) = \infty, \quad r < d(\omega_1\omega_2)$$
$$= 0, \quad r > d(\omega_1\omega_2), \quad (43)$$

where $d(\omega_1, \omega_2)$ is the distance of closest approach between two HGO's and is given by

$$d(\omega_1\omega_2)/d_0 = \sigma(\omega_1\omega_2)/\sigma_0. \quad (44)$$

Here, $\sigma(\omega_1\omega_2)$ is given by eq. (3).

In order to be consistent with the calculation of the perturbation terms discussed in the previous section, we use the decoupling approximation to estimate the reference and perturbation parts of the GOCE model.

For the GOCE model, Singh *et al* [12] have given an expression for $d_0^* = d_0/\sigma_0$

$$d_0^* = d_B^*/[1 - (\sigma_{11}/2\sigma_{00})\delta] \approx d_B^*(1 + (\sigma_{11}/2\sigma_{00})\delta), \quad (45)$$

where

$$d_B^* = \int_0^\omega (1 - \exp[-\beta u_0(r^*)])dr^*, \quad (46a)$$

$$\delta = \int_0^\omega ((r^*/d_B^*) - 1)^2(d/dr^*)(\exp[-\beta u_0(r^*)])dr^*, \quad (46b)$$

$$\sigma_{00} = (1 - \eta/2)(1 - \eta)^{-3}, \quad (47a)$$

$$\sigma_{11} = (2 - 7.5\eta + 0.5\eta^2 + 5.7865\eta^3 - 1.51\eta^4)(1 - \eta)^{-4}, \quad (47b)$$

with

$$\eta = \rho V_{HGO} = (\pi/6)\rho^* d_0^{*3} K \quad (48)$$

as the packing fraction.

The thermodynamic function of the reference system can be determined from the equation of state of the reference system, given by [12]

$$P_0/\rho kT = (P_{HGO}/\rho kT) + 4\eta\delta F_0(\chi)$$
$$[(\tau_2/2) - (\sigma_{11}/2\sigma_{00})\tau_1], \quad (49)$$

where [17,18]

$$P_{HGO}/\rho kT = 1 + (2\eta(2 - \eta)/(1 - \eta)^3)F_0(\chi), \quad (50)$$

$$F_0(\chi) = (1 - \chi^2)^{1/2}[1 - (\chi^2/6) - (\chi^4/40) - (\chi^6/112) - ...]. \quad (51)$$

$$\tau_1 = \sigma_{00} + \sigma_{11}, \quad (52a)$$

$$\tau_2 = 2\sigma_{11} + \sigma_{22}, \quad (52b)$$

σ_{00} and σ_{11} are given by eq. (47) and

$$\sigma_{22} = (2 - 2\eta + 3\eta^2 + 0.17\eta^3 - 26.797\eta^4 + 11.22\eta^5)(1 - \eta)^{-5}. \quad (53)$$

The residual Helmholtz free energy of the reference system is given by [12]

$$(A_0 - A^*)/NkT = A_{HGO} - A^*/NkT + 4\delta F_0(\chi)(\beta\Delta f), \quad (54)$$

where

$$(A_{HGO} - A^*)/NkT = \eta(4 - 3\eta)(1 - \eta)^{-2}F_0(\chi), \quad (55)$$

$$\beta\Delta f = 3\eta^2(1 + 1.75\eta - 5.249\eta^2)(1 - \eta)^{-3}. \quad (56)$$

We use eqs. (49) and (54) respectively to calculate the pressure P_{GO} and the residual free energy $(A_{GO} - A^*)$ of the reference fluid for the GOCE model. The configurational internal energy for the reference system is obtained from eq. (54).

The first order perturbation correction to the free energy is given by [12]

$$A_1 / NkT = (12\eta_\omega / T^*)F_0(\chi)A_1^*,$$ (57)

where

$$A_1^* = l_1 - l_2 - l_2^0$$ (58)

with

$$I_1 = 4\int_1^\infty dr^* r^{*2}[(d_\omega^* r^*)^{-12} - (d_\omega^* r^*)^{-6}]Y_{HS}(r^*, \eta_\omega),$$ (59a)

$$I_2 = 4\int_1^{r_{min}^*/d_\omega^*} dr^* r^{*2}[(d_\omega^* r^*)^{-12} - (d_\omega^* r^*)^{-6}]Y_{HS}(r^*, \eta_\omega),$$ (59b)

$$I_2^0 = \int_1^{r_{min}^*/d_\omega^*} dr^* r^{*2}Y_{HS}(r^*, \eta_\omega),$$ (59c)

$$\eta_\omega = \eta - \eta^2 / 16,$$ (60a)

$$d_\omega^{*3} = d^{*3}\eta_\omega / \eta.$$ (60b)

The values of Y_{HS} (r^*) are calculated from the hard sphere values [9] of the Y-function, defined as

$$Y(r^*) = \exp[\beta u(r^*)]g(r^*).$$ (61)

4. Results and discussion

In order to test the theory for predicting the thermodynamic properties of the non-spherical molecule fluid, simulation data are needed. But as far as we know, there are no simulation data for the thermodynamic properties involving the GOCE model. Hence, we use experimental data to make our comparisons. However, only few fluids such as N_2, CO_2 and C_6H_6 are characetrised by the GOCE (or GO) model. But the experimental data of C_6H_6 are not available. In the present paper, we calculate the thermodynamic properties of N_2 and CO_2 which can be characterised by the GOCE model. Their force parametrs are reported in Table 2. The GOCE

Table 2. Force parameters for N_2 and CO_2 using the GOCE potential model

System	K	σ_0/Å	$(\varepsilon_0/k)K^{-1}$	$\alpha/10^{-4}$ cm³	$Q/10^{-b}$ e s u.cm³
N_2	1 30	3.370	94.00	1.730	−1 40
CO_2	1.88	2.853	285 81	2.925	4 30

parameters (σ_0, ε_0 and K) for N_2 and CO_2 are taken from the literature [19,2]. For CO_2, $l^* = l/\sigma = 0.815$ [2], which corresponds to the Centre-to-Centre distances of the outermost atoms. Corresponding to this values of l^*, $K = 1.88$, which is used in the present calculation. In addition, this table include the parameters (α,Q), taken from Shukla et al [20]. They used these parameters with usual LJ (12−6) potential model.

The magnitude of the contribution of various branches of pair interactions to the residual Helmholtz free energy for N_2 are given in Table 3 for $p^* = 0.659$, $T^* = 0.957$, $p^* = 0.603$,

Table 3. Comparison of magnitude of contributions of various branches of pair potentials to the residual free energy for N_2 at K = 1 3

Contributions	$p^* = 0.659$ $T^* = 0.957$	$p^* = 0.659$ $T^* = 1.064$	$p^* = 0.659$ $T^* = 1.170$
$A_1(in)/NkT$	−0.05216	−0.04049	−0.03676
$A_2(Perm)/NkT$	−0.12125	−0.08386	−0.06968
A_{12}/NkT	0.00214	0.00132	0.00102
A_{13}/NkT	0.00667	0.00337	0.00241
A_3/NkT	0.00881	0.00469	0.00343
$\Delta A/NkT$	−0.16520	−0.11991	−0.10317
$(A_{GO} - A^*)/NkT$	−2.47006	−1.98830	−1.56884
$(A - A^*)/NkT$	−2.63526	−2.10821	−1.67201

$T^* = 1.064$ and $p^* = 0.598$, $T^* = 1.170$. It may be seen from the table that the contribution in the first order perturbation is small. In the second order perturbation term, the contributions arising from quadrupole moment interaction to the free energy is significant. The contribution of the third order perturbation term is small in comparison to the contribution arising in the second order terms. This shows the convergence of the series. The third order terms includes A_{32} and A_{33} terms. Their contributions are comparable in magnitude. The higher order terms are taken approximately into account by using Padé' approximant [16].

It is clear from this table that the main contribution to the free energy comes from the reference GOCE model.

The calculated values of the thermodynamic properties such as residual internal energy $U^c / NkT = (U - U^*)/NkT$, entropy S/Nk and the pressure P for N_2 are compared with experimental data [21−23] in Table 4. The results obtained by Shukla et al [20] are also reported there. The agreement between theory and experiment are found to be good, sometime better than one obtained by Shukla et al.

The calculated values of U^c/NkT and S/Nk for CO_2 are compared with experimental data [21−23] as well as with those of Shukla et al [20] in Table 5. Even in this case the agreement is fairly good.

Table 5. Thermodynamic properties of CO_2 at K = 1 88.

T(K)	(mol/l)	$-U^c/NkT$			$-S/Nk$		
		Present work	Shukla et al[20]	Expt. [21-23]	Present work	Shukla et al[20]	Expt. [21-23]
223 2	26.209	7.446	7.426	7.465	4 109	4.196	4.069
233.2	25 337	6 902	6 816	6 862	3 722	3 795	3 684
243.2	24.408	6.304	6 158	6.293	3.350	3 353	3.356
253.2	23 400	5 724	5.681	5.761	3.006	3.064	3 076
263.2	22 313	5.203	5 168	5.256	2.793	2.729	2.781
273.2	21 118	4.786	4.669	4.763	2.465	2.407	2 445
283.2	19.614	4 303	4 159	4.264	1.998	2 067	2.072
293.2	17 609	3.722	3.697	3.731	1.673	1 696	1.634
303.2	13.475	2.933	2.714	2.841	1 095	1.117	1 079

Table 4. Thermodynamic properties of N_2 at $K = 1.3$

ρ (mol/l)	$-U^*/NkT$			S/Nk			P/atom		
	Present work	Shukla et al [20]	Expt. [21-23]	Present work	Shukla et al [20]	Expt. [21-23]	Present work	Shukle et al [20]	Expt [21 ?]
T = 90 K									
26.63	6 132	6.193	6.146	2 970	2 999	3.005	10.11	10 00	10
26.89	6.205	6.219	6.212	3 044	3 043	3.060	30.27	30 00	30
27.14	6.240	6.289	6 274	3 100	3 108	3.109	51 06	51.00	50
27.69	6.348	6 349	6 415	3.212	3 201	3 22	101.29	101 00	100
28.59	6 538	6 412	6 632	3.387	3.381	3 39	201 14	202 00	200
29.96	6.815	6 413	6.924	3.662	3 659	3 658	403.98	405.00	400
30.97	7.008	6.598	7 118	3.865	3 859	3 884	596 44	609 00	600
T = 100 K									
24.57	5.051	5.071	5.060	2 628	2 643	2 630	7 80	7 68	7 7
24.59	5.076	5 074	5.090	2.638	2 646	2.640	10.03	10 05	10
25 01	5.143	5.134	5.166	2 703	2.715	2 698	30.32	30 52	30
25.37	5.247	5.182	5.240	2 760	2 775	2.759	49.98	50 03	50
26.14	5 392	5.378	5.402	2.893	2.909	2.888	100.46	100.56	100
27.29	5 620	5.583	5 648	3 084	3 060	3.093	200 96	201 76	200
28 88	5.920	5 890	5.953	3 367	3.374	3.363	402.52	402 26	400
30.04	6.073	5.995	6.151	3 650	3 607	3.693	601.67	604.91	600
T = 110 K									
22.18	4.114	4.181	4 120	2 199	2.205	2.200	14.70	12 15	14 5
22.73	4 271	4 262	4.267	2 315	2.301	2.328	30 39	30.38	30
23.32	4 392	4.346	4.387	2 387	2.385	2.423	50.12	50 17	50
24.46	4 607	4.500	4 578	2 569	2.558	2 571	100 50	101.68	100
25.93	4.859	4.832	4 850	2.808	2.800	2.798	200 46	202.54	200
27 82	5.166	4 879	5 168	3 078	3 143	3 081	402.45	404 32	400
29 12	5.361	5 295	5.374	3 233	3 364	3 118	600 92	619.16	600

5. Concluding remarks

In this paper, we develop the perturbation theory, where the GOCE potential is taken as a reference and multipole moment and induced interactions as a perturbation to estimate the thermodynamic function of molecular fluid of non-spherical molecules. The properties of the reference GOCE fluid are calculated using the WCA type perturbation theory developed by Singh et al [12]. The perturbation terms are expressed in terms of J and I integrals, which can be easily evaluated. We have applied this theory for N_2 and CO_2 only and found good agreement with the experimental data.

This theory can be applied to estimate the thermodynamic functions of any system whose GO parameter (σ_0, ε_0 and K) are accurately known.

Acknowledgments

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