The VIM Theory of Molecular Thermodynamics

Part I: Analytic Equation of State of Nonpolar Fluids

Variational inequality minimization (VIM) theory of statistical mechanics is used to derive analytic equations of state for nonpolar fluids. Pair- and triplet-intermolecular potential energy functions are taken into account in the formulation of this equation of state. The VIM theory has made it possible to derive rather simple expressions for the thermodynamic properties of nonpolar fluids. Predictions of the thermodynamic properties of argon and methane in the liquid phase, in the vapor phase, and in the critical region by the VIM equation of state are shown to be in excellent agreement with the experimental data.

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SCOPE

Majority of the equations of state which are used for engineering design computations are empirical correlations that are applicable only for interpolation purposes in the range of experimental data on which they are built. The existing statistical mechanical equations of state, even though are more versatile than the empirical equations of state, are generally too complicated to be used for engineering design calculations.

The objectives of this study has been to utilize the modern theories of statistical mechanics to develop algebraically analytic and accurate equations of state to be used in engineering design calculations. The resulting equations of state are intended to be applicable for both the liquid phase and the vapor phase. For nonpolar fluids this task has been accomplished by utilizing the variational inequality minimization (VIM) theory of statistical mechanics and development of a new technique for derivation of the potential energy parameters and the expression for the hard-sphere reference diameter as the variational parameter.

CONCLUSIONS AND SIGNIFICANCE

This paper demonstrates that through the variational inequality minimization technique it is possible to produce algebraically analytic equations of state for nonpolar fluids which are accurate and are based on statistical mechanical grounds. It is also shown that the resulting equations of state are equally accurate for prediction of PVT, enthalpy, and heat capacities of nonpolar fluids in both the liquid and vapor phases. The VIM equation of state is used for prediction of thermodynamic properties of argon and methane. Comparisons of the results of the VIM equation of state with the experimental data indicate that this equation of state can accurately predict all the thermodynamic properties. Also the VIM equation of state is simple enough to be used for engineering design calculations. Development of the VIM equation of state of nonpolar fluids is the groundwork for the construction of similar analytic equations of state for polar fluids, quantum fluids, and associated molecular fluids which are of more practical interest for engineering design calculations.

BACKGROUND AND THEORY

Statistical mechanical approach to the equilibrium behavior of a substance (gas, liquid or solid) can be represented by formulation of the partition function in the canonical ensemble. The basic relation of the statistical mechanical description of the canonical ensemble is that between the Helmholtz free energy A and the canonical partition function PF of an N-particle system confined in a volume V and at a temperature T (Hirschfelder et al., 1967)

$$A = -kT\,ln\,PF, \tag{1}$$

$$PF = PF_{\text{int}}\cdot Q, \tag{2}$$

$$Q = \frac{1}{N!}\int ..N.. \int \exp(-\underline{\phi}/kT)d\mathbf{r}_1 \ldots d\mathbf{r}_N. \tag{3}$$

where PF_{int} is the partition function of the N molecules due to their internal degrees of freedom, Q is the configurational integral, and $\underline{\phi}$ is the total intermolecular potential energy function. Let us choose two different systems, both with the same volume, temperature, and number of molecules, but with different potential energy functions. The ratio of the configurational integrals of these two systems can then be written as

$$\begin{aligned} Q/Q_o &= \int ..N.. \int e^{-\underline{\phi}_o/kT}\cdot e^{(\underline{\phi}_o-\underline{\phi})/kT}d\mathbf{r}_1 \ldots d\mathbf{r}_N/ \\ &\qquad \times \int ..N.. \int e^{-\underline{\phi}_o/kT}d\mathbf{r}_1 \ldots d\mathbf{r}_N \\ &= \langle e^{(\underline{\phi}_o-\underline{\phi})}/kT\rangle_o. \end{aligned} \tag{4}$$

According to this equation the ratio of configurational integral of one system over the other (which we will define as the reference

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system) is equal to the statistical mechanical expectation value of $(\underline{\phi}_o - \underline{\phi})/kT$ over the reference system. The righthand side of Eq. 4 can be expanded about the value of $\langle(\underline{\phi}_o - \underline{\phi}\rangle_o\rangle_o$ by the Taylor's theorem with the following truncated result,

$$\langle e^{(\underline{\phi}_o-\underline{\phi})/kT}\rangle_o = \exp\langle(\underline{\phi}_o - \underline{\phi})/kT\rangle_o + \frac{1}{2}\langle[(\underline{\phi}_o - \underline{\phi})/kT - \langle(\underline{\phi}_o - \underline{\phi})/kT\rangle_o]^2 e\xi\rangle_o, \quad (5)$$

where

$$(\underline{\phi}_o - \underline{\phi})/kT \leq \xi \leq \langle(\underline{\phi}_o - \underline{\phi})/kT\rangle_o. \quad (6)$$

The second term in the righthand side of Eq. 5 is always a positive value. As a result, by removing this term from Eq. 5 we will produce an inequality which after replacing in Eq. 4 will assume the following form

$$Q/Q_o = \exp\langle(\underline{\phi}_o - \underline{\phi})/kT\rangle_o, \quad (7)$$

or with respect to the configurational Helmholtz free energy it will be

$$A^{\text{con}} \leq A_o^{\text{con}} + \langle\underline{\phi} - \underline{\phi}_o\rangle_o. \quad (8)$$

Inequality 7 is known as the Gibbs-Bogoliubov inequality (Mansoori and Canfield, 1969; Girardeau and Mazo, 1973). In its quantum mechanical form, this inequality has been used in a variety of quantum problems. However, its application in statistical mechanics and engineering computations is now being realized. According to this inequality, provided that we know thermodynamic and intermolecular properties of a reference system, and with the knowledge about the intermolecular potential energy function of a nonsimple system, we may minimize the righthand side of this inequality to calculate the Helmholtz free energy and other thermodynamic properties of the nonsimple system. During the past one and a half decade this variational concept has been applied for prediction of the thermodynamic properties of nonpolar, polar, ionic, and metallic systems with varying degrees of success (Mansoori and Canfield, 1970; Stell et al., 1972; Rasaiah and Stell, 1970; Shimoji, 1977). It has also been used successfully for mixture calculations and prediction of melting transition of crystalline solids to liquids (Mansoori and Canfield, 1969-II; Buchanan, 1974). In the present report we introduce a computational scheme, based on the Gibbs-Bogoliubov inequality for the development of accurate and algebraically analytic equations of state of nonpolar fluids such as argon and methane. This is achieved because of the special feature of the Gibbs-Bogoliubov inequality when a hard-sphere fluid is chosen as the reference system and the ability of expressing the hard-sphere reference diameter linearly with respect to density and inverse temperature. The analytic equations of state presented here can be readily applied for engineering process design calculations. In subsequent publications we will introduce extensions of this technique to the case of polar fluids, such as carbon dioxide and methyl chloride.

In the case when two- and three-body interaction potential energy functions are considered, the total potential energy function can be written as (Rowlinson, 1969)

$$\underline{\phi} = \sum_{i>j=1}^{N}\sum \phi_{ij} + \sum_{i>j>k=1}^{N}\sum\sum \psi_{ijk}, \quad (9)$$

where ϕ_{ij} is the pair potential and ψ_{ijk} is the triplet interaction potential. Now with the use of the hard-sphere model of diameter d as the reference fluid, with

$$\phi_o = \begin{cases} \infty \text{ for } r_{ij} \leq d \\ 0 \text{ for } r_{ij} > d \end{cases}, \quad (10)$$

and introduction of the concept of pair- and triplet-distribution functions of the hard-sphere reference, g_{o2}, g_{o3}, in inequality 8, we will derive the following inequality for the Helmholtz free energy

$$A \leq A_o + A_{2b} + A_{3b}, \quad (11)$$

where A_o is the hard-sphere reference Helmholtz free energy and

$$A_{2b} = \iint g_{o2}(\mathbf{r}_{12})\phi(\mathbf{r}_{12})d\mathbf{r}_1 dr_2 \quad (12)$$

and

$$A_{3b} = \int\int\int g_{o3}(123)\psi(123)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (13)$$

To utilize inequality 11 for calculation of the Helmholtz free energy and other thermodynamic properties of fluids, its righthand side should be minimized with respect to d according to the following conditions

$$A' = (\partial A_o/\partial d)_{\rho,T} + (\partial A_{2b}/\partial d)_\rho + (\partial A_{3b}/\partial d)_\rho = 0, \quad (14)$$

$$A'' = (\partial^2 A_o/\partial d^2)_{\rho,T} + (\partial^2 A_{2b}/\rho d^2)_\rho + (\partial^2 A_{3b}/\partial d^2)_\rho > 0. \quad (15)$$

Equation 14 in conjunction with condition 15 is usually used to find a temperature- and density-dependent relation for the hard-sphere reference diameter (Mansoori and Canfield, 1969-I)

$$d = d(\rho,T), \quad (16)$$

as the variational parameter. This procedure can be used for the accurate prediction of properties of simple fluids for which their potential energy functions are pairwise and close to a hard-sphere model and with exact knowledge about their potential energy parameters. For realistic fluids, inequality 10 with the procedure for the hard-sphere reference diameter calculation explained above does not usually predict the Helmholtz free energy accurately. Instead, we obtain a least-upperbound to the Helmholtz free energy which may, or may not, result in the accurate prediction of the other thermodynamic properties. In addition, due to the large discrepancy between the reported pair-potential energy parameters of molecules in the literature, and the lack of data for the triplet potential energy parameters of realistic molecules, the variational scheme proposed below may be used for real fluids. This new computational scheme, in addition to producing a universal and simple relation for the hard-sphere reference diameter, as a function of temperature and density, also provides us the means of calculating a set of consistent pair- and triplet-interaction potential energy parameters.

According to Carnahan and Starling (1969) the Helmholtz free energy function of a hard-sphere reference fluid is given by

$$A_o = A^{ig} + RT\eta(4 - 3\eta)/(1 - \eta)^2, \quad (17)$$

where

$$\eta = \frac{\pi}{6}\rho N_a d^3, \quad (18)$$

is a dimensionless density and N_a is the Avogadro's number. Provided we know the hard-sphere diameter in the form of Eq. 16 which would give the minimum of the righthand side of inequality 11, we could then write

$$A = A^{ig} + RT\eta(4 - 3\eta)/(1 - \eta)^2 + A_{2b}(\rho,d) + A_{3b}(\rho,d) \quad (19)$$

From Eq. 19 we can derive relations for the other thermodynamic properties such as entropy, internal energy, enthalpy, and heat capacities. In general, we will need to know A_{2b} and A_{3b} terms to calculate thermodynamic properties. However, this is not necessary for calculation of entropy. According to thermodynamics

$$S = -(\partial A/\partial T)_\rho \quad (20)$$

Replacing Eq. 19 in Eq. 20 and with consideration of the variational condition 14 we conclude that

$$S(\rho,T) = S^{ig} - R\eta(4 - 3\eta)/(1 - \eta)^2 = S_o(\eta) \quad (21)$$

According to this relation entropy of a real fluid is equivalent to the entropy of a hard-sphere fluid provided that an appropriate

TABLE 1. COEFFICIENTS OF EQ. 23, HARD-SPHERE DIAMETER, OF ARGON AND METHANE $d[10^{-10}\text{m}] = a_o + a_1\rho[\text{mol/L}] + a_2/T[\text{K}] + a_3\rho[\text{mol/L}]/T[\text{K}]$

	Argon	Methane
a_o	3.1885	3.6999
a_1	−0.00811	−0.00641
a_2	26.3250	24.5914
RMSD	0.003	0.013
Fluid Entropy Data	(i)	(iii)
Ideal Gas Entropy Data	(ii)	(iv)

(i) Vargaftik (1975); (ii) Din (1961); (iii) Goodwin (1974); (iv) McDowell and Kruse (1963).

temperature- and density-dependent hard-sphere diameter for the reference hard-sphere molecules is chosen which will satisfy variational conditions 14 and 15. Due to the simplicity of Eq. 21 it can be used to calculate η (or d) from the experimental entropy data of a fluid. Solving Eq. 21 for η results in the following expression

$$\eta = \frac{\pi}{6}\rho N_a d^3 = \{2 - (S - S^{ig})/R + [4 - (S - S^{ig})/R]^{1/2}\}/\{3 - (S - S^{ig})/R\} \quad (22)$$

By application of entropy data of different fluids, Eq. 22 can be used to calculate the hard-sphere reference diameter d vs. density and temperature. Computation of the hard-sphere diameter for varieties of fluids indicate that it is linearly dependent on density and inverse temperature for both the vapor and liquid phases. For a given fluid the hard-sphere diameter can be accurately represented by the following expression,

$$d(\rho,T) = a_o + a_1\rho + a_2/T + a_3\rho/T. \quad (23)$$

Numerical values of coefficients a_i for argon and methane are in Table I.

Due to the availability of a simple and accurate relation for the hard-sphere reference diameter, Eq. 23, one would not need any more to calculate this parameter from inequality 11. However, since this parameter accurately correlates the experimental entropy data we can safely assume that it will minimize the righthand side of inequality 11. This assumption could be tested when accurate potential energy functions and potential energy parameters are available for the molecular fluids under consideration. However, in the absence of such accurate intermolecular data we may safeguard the correctness of the assumption by choosing the potential parameters such that conditions 14 and 15 are satisfied. This can be accomplished by considering Eqs. 14 and 15 as constraints in calculation of the potential energy parameters of model potentials from the experimental PVT or any other experimental thermodynamic data. This will also alleviate the difficulty which is associated with the sparsity of intermolecular potential parameters data which sometimes widely vary from one literature to another. Once the intermolecular potential energy parameters are calculated, the hard-sphere reference diameter, Eq. 23, can be transformed to a dimensionless (univeral) form which would then be applicable for hard-sphere diameter of other molecules.

ANALYTIC VIM EQUATION OF STATE

For nonpolar molecules the pair-intermolecular potential energy function can be represented by the Lennard-Jones potential energy function (Hirschfelder et al., 1967; Rowlinson, 1969)

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (24)$$

The triplet-interaction potential energy function is shown to be overwhelmingly represented by the Axilrod-Teller triple-dipole interaction function (Rowlinson, 1969)

$$\psi(123) = \nu(1 + 3\cos\theta_1\cos\theta_2\cos\theta_3)/(r_{12}r_{13}r_{23})^3, \quad (25)$$

where θ_i's and r_{ij}'s are the angles and sides of the triangle joining the centers of the three interacting molecules, respectively, and ν is a constant.

By replacing Eq. 24 in Eq. 12 we get

$$A_{2b} = (N\epsilon)48\eta[c^{-12}I_{12}(\eta) - c^{-6}I_6(\eta)], \quad (26)$$

where

$$I_n(\eta) = \int_1^\infty g_{o2}(x,\eta)x^{2-n}dx, \quad (27)$$

$c = d/\sigma$, and $x = r/d$. Mansoori and Ali (1974) have shown that $I_n(\eta)$ can be accurately represented by a polynomial of the form

$$I_n(\eta) = \sum_{i=0}^{5} C_{ni}\eta^i. \quad (28)$$

In the present report we have recalculated $I_n(\eta)$ for different values of $n(= 6 \text{ to } 14)$ with the use of Perram's (1978) recommended, and exact, hard-sphere radial distribution function. Coefficients C_{ni} resulting from this recomputation are reported in Table 2, together with the RMSD and maximum percentage deviation of Eq. 28 from Eq. 27.

Barker and coworkers (1968) have derived the following algebraic expression for A_{3b} by replacing Eq. 25 in Eq. 13 and performing, both, computer simulation and direct numerical integration using Kirkwod's supperposition approximation for g_{o3},

$$A_{3b} = \frac{N}{d^9}(f_1/f_2); \quad (29)$$

$$f_1 = 5.17184\eta + 6.16139\eta^2 - 2.19927\eta^3 \quad (30)$$

$$f_2 = 1 - 1.12789\eta + 0.73166\eta^2 \quad (31)$$

Now, by replacing Eqs. 26 and 29 in Eq. 19, the following analytic expression for the Helmholtz free energy will be resulted

$$A/RT = A^{ig}/RT + \eta(4 - 3\eta)/(1 - \eta)^2 + \frac{48\eta}{T^*}[c^{-12}I_{12}(\eta) - c^{-6}I_6(\eta)] + \frac{\nu^*}{T^*}c^{-9}(f_1/f_2) \quad (32)$$

where

$$\nu^* = \frac{\nu}{\epsilon\sigma^9}\,. \quad (33)$$

TABLE 2. COEFFICIENTS C_{ni} OF POLYNOMIAL 28 REPRESENTING INTEGRAL 27 FOR DIFFERENT VALUES OF EXPONENT n (6,8,10,12,14), AND % ROOT-MEAN-SQUARE DEVIATION AND MAXIMUM % DEVIATION OF EQ. 28 FROM 27

i	C_{6i}	C_{8i}	C_{10i}	C_{12i}	C_{14i}
0	0.3340	0.1996	0.1437	0.1075	0.0553
1	0.4064	0.3447	0.2349	0.3113	0.1296
2	0.5370	0.1300	0.6364	−0.2146	0.1073
3	−0.8516	0.9585	−0.8158	1.2176	0.7443
4	1.2603	−1.7826	1.5070	0.0000	−1.0469
5	0.0000	2.0074	0.0000	0.0000	1.5752
RMSD	0.018	0.005	0.02	0.103	0.002
Max. % Dev.	0.069	0.027	0.190	0.143	0.044

By using the relationship between pressure and the Helmholtz free energy

$$P = \rho^2(\partial A/\partial \rho)_T$$

and application of condition 14, the following analytic expression for the compressibility factor will be derived

$$Z = P/\rho RT = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 + \frac{48\eta}{T^*}\left[c^{-12}\{I_{12}(\eta) + J_{12}(\eta)\} - c^{-6}\{I_6(\eta) + J_6(\eta)\}\right] + \frac{\nu^*}{T^* c^9}\left(\frac{f_1' f_2 - f_1 f_2'}{f_2^2}\right) \quad (34)$$

where

$$J_n(\eta) = \sum_{i=0}^{5} i C_{ni}\eta^i. \quad (35)$$

$$f_1' = 5.17184 + 12.32278\eta - 6.59781\eta^2, \quad (36)$$

$$f_2' = -1.12789 + 1.46332\eta. \quad (37)$$

Supposing we know the potential energy parameters ϵ, σ and ν, and the hard-sphere diameter of a fluid, Eq. 34 can be used for calculation of pressure of a fluid at different temperatures and densities. However, accuracy of PVT predictions by Eq. 34 is very sensitive to the values of the potential parameters. The potential energy parameters reported in the literature are rather sparse and inconsistent. To apply Eq. 34 for the accurate thermodynamic prediction of nonpolar fluids potential energy parameters should be recalculated according to the following procedure:

Parameters ϵ, σ and ν appearing in Eq. 34 may be considered as three adjustable parameters for fitting the experimental compressibility (or any other thermodynamic property) data to Eq. 34. But, since these parameters should also be chosen such that conditions 14 and 15 will be satisfied, we will need to minimize

$$\sum_{j=1}^{n} (Z_j^{\text{exptl}} - Z_j)^2 \quad (38)$$

with the following constrains

$$\sum_{j=1}^{n} A_j' = 0; \quad \sum_{j=1}^{n} A_j'' > 0, \quad (39)$$

where Z_j^{exptl} is the experimental compressibility data, Z_j is compressibility as calculated by Eq. 34, A_j' and A_j'' are given by Eqs. 14 and 15, respectively, all for the jth data point, and n is the number of data points used. This minimization problem can be formulated and solved by introduction of a Lagrangian multiplier λ such that

$$\sum_{j=1}^{n} (Z_j^{\text{exptl}} - Z_j)^2 + \lambda \sum_{j=1}^{n} A_j' = \text{minimum}, \quad (40)$$

with respect to ϵ, σ and ν. The choice of an appropriate set of experimental PVT data minimization of Eq. 40 will produce the numerical values for the potential energy parameters. In the present work only the dense fluid PVT data of argon (Vargaftik, 1975) and methane (Goodwin, 1974) are used for calculation of the potential energy parameters. Table 3 shows the values of these parameters for argon and methane as calculated by the present technique along with the other literature values for these parameters. It is clear that the present results are in the range of the values calculated based on the second virial coefficients data. However, due to the sensitivity of equations of state to these parameters and the sparsity of the literature data, results of the present work should be used for the VIM equation of state calculations.

Availability of the expression for the hard-sphere diameter and the potential energy parameters for argon and methane allows us to formulate a universal (dimensionless) formula for the hard-sphere diameter as:

$$c = \frac{d}{\sigma} = \alpha_o + \alpha_1\rho^* + \alpha_2/T^* + \alpha_3\rho^*/T^* \quad (41)$$

TABLE 3. POTENTIAL ENERGY PARAMETERS OF ARGON AND METHANE CALCULATED BY PRESENT TECHNIQUE

	Argon	Methane
ϵ/k [K]	115.9 (119.0)*	144.9 (148.4)*
$\sigma[10^{-10}\text{m}]$	3.412 (3.438)*	4.002 (3.812)*
$\nu/k[10^{-94}\text{m}^9\cdot\text{K}]$	6.385	47.897

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* Based on the second virial coefficient data (Edalat et al., 1980).

where

$$\alpha_0 = 0.95805 - 2.66653\nu^*,$$

$$\alpha_1 = -0.23650 + 15.52709\nu^*,$$

$$\alpha_2 = 0.12490 - 6.56851\nu^*,$$

$$\alpha_3 = -0.09520 + 4.55369\nu^*,$$

Equations 34 and 41 constitute the universal analytic VIM equation of state of nonpolar fluids. From Eqs. 32 and 34 analytic expressions for the other thermodynamic properties of nonpolar fluids can be also derived. Expression for the internal energy can be derived from Eq. 32 through the thermodynamic relation

$$U/T^2 = -[\partial(A/T)/\partial T]_\rho$$

and application of condition 14. The result will be

$$U/RT = U^{ig}/RT + \frac{48\eta}{T^*}[c^{-12}I_{12} - c^{-6}I_6] + \frac{\nu^*}{T^*}\ c^{-9}(f_1/f_2). \quad (42)$$

From thermodynamic equation $H = U + PV$ and application of Eqs. 34 and 42, the expression for enthalpy can be derived:

$$H/RT = H^{ig}/RT + \frac{2\eta(2 - \eta)}{(1 - \eta)^3} + \frac{48\eta}{T^*}\left[c^{-12}\{2I_{12}(\eta) + J_{12}(\eta) = \} - c^{-6}\{2I_6(\eta + J_6(\eta))\}\right] + \frac{\nu^*}{T^*}[(f_1 f_2 - f_1' f_2 + f_1 f_2')/f_2^2]. \quad (43)$$

From the expression for the internal energy, Eq. 42, and the thermodynamic relation $C_v = (\partial U/\partial T)_\rho$ the following analytic expression for the heat capacity at constant temperature will be derived

TABLE 4. DENSITY AND COMPRESSIBILITY OF ARGON AS CALCULATED BY VIM EQUATION OF STATE, EQ.34, AND COMPARED WITH EXPERIMENTAL (VARGAFTIK, 1975) DATA

T [K]	P $[\text{Nm}^{-2}] \times 10^5$	ρ_{exptl} [mol/L]	ρ_{cal} [mol/L]	Z_{exptl}	Z_{cal}
90.0	100.0	35.168	35.926	0.380	0.372
140.0	100.0	26.603	26.848	0.323	0.320
100.0	200.0	34.495	34.316	0.697	0.701
140.0	200.0	28.711	27.894	0.598	0.616
160.0	200.0	25.256	24.769	0.595	0.607
100.0	300.0	35.149	35.797	1.027	1.008
120.0	300.0	32.697	32.126	0.920	0.936
140.0	300.0	30.084	29.524	0.857	0.873
180.0	300.0	24.450	23.836	0.820	0.841
120.0	400.0	33.467	33.607	1.198	1.193
140.0	400.0	31.132	31.044	1.104	1.107
160.0	400.0	28.701	28.747	1.048	1.046
180.0	400.0	26.299	26.077	1.016	1.025
120.0	500.0	34.133	34.851	1.468	1.438
140.0	500.0	31.987	32.445	1.343	1.324

TABLE 5. DENSITY AND ENTHALPY OF METHANE AS CALCULATED BY VIM EQUATION OF STATE AND COMPARED WITH EXPERIMENTAL (GOODWIN, 1974) DATA

T [K]	P [Nm^{-2}] × 10^5	ρ_{exptl} [mol/L]	ρ_{cal} [mol/L]	H_{exptl} [J/mol]	H_{cal} [J/mol]
170.0	60.0	20.440	20.468	14,634.0	14,821.5
	80.0	20.863	21.018	14,610.0	14,710.0
	150.0	21.952	22.082	14,556.0	14,438.0
160.0	16.0	20.982	20.918	14,296.0	14,387.0
	40.0	21.467	21.341	14,275.0	14,262.5
	80.0	22.104	22.200	14,254.0	14,101.0
	200.0	23.437	23.610	14,242.0	13,776.0
	400.0	24.899	25.089	14,301.5	13,441.0
150.0	40.0	22.739	22.894	13,648.0	13,648.0
	80.0	23.213	23.378	13,649.0	13,529.0
	200.0	24.301	24.525	13,681.0	13,269.5
140.0	40.0	23.859	23.815	13,237.0	13,067.0
	80.0	24.229	24.235	13,254.0	12,975.0
	200.0	25.131	25.209	13,322.0	12,758.5
130.0	16.0	24.683	24.509	12,622.0	12,538.0
	60.0	25.028	25.165	12,652.0	12,453.0
	100.0	25.312	25.411	12,682.0	12,384.0
	300.0	26.463	26.671	12,851.0	12,120.0
120.0	60.0	25.942	25.922	11,466.0	11,887.0
	100.0	26.178	26.089	11,506.0	11,829.0
	150.0	26.452	26.474	11,555.5	11,766.0
	300.0	27.174	27.418	11,710.0	11,605.0
110.0	60.0	26.806	26.899	11,321.5	11,329.0
	100.0	27.005	27.193	11,368.0	11,283.0

$$\frac{C_v - C_v^{ig}}{R} = (48\eta/T_*^2)\left[-\frac{3}{c}(\alpha_2 + \alpha_3\rho^*)\right][c^{-12}\{3I_{12}(\eta) - J_{12}(\eta)\} - c^{-6}\{I_6(\eta) - J_6(\eta)\}] + (\nu c^{-9}/T_*^2) \times \left[-\frac{3}{c}(\alpha_2 + \alpha_3\rho^*)\right][(3f_1f_2 - f_1'f_2 + f_1f_2')/f_2^2]. \quad (44)$$

Expression for the heat capacity at constant pressure $C_p = (\partial H/\partial T)_P$ can be derived with the use of the following thermodynamic expression

$$C_p = C_v + T(\partial P/\partial T)_\rho^2/\rho^2(\partial P/\partial \rho)_T$$

and application of Eqs. 34 and 44. However, the algebraic expression for C_p is rather lengthy and it will not be reported here.

In this paper, thermodynamic properties of argon and methane are predicted by the VIM equation of state. Table 4 contains compressibility and density data of argon predicted by the VIM equation of state at low temperatures; agreement of predictions with the experimental data is quite good. Table 5 contains density and enthalpy of methane as predicted by the VIM equation of state and compared with the data produced by the accurate Goodwin correlation on methane (Goodwin, 1974); agreement of the VIM theory with the experimental data is also good. Saturation curve and different isobars of methane in liquid and vapor phases are shown in Figure 1 as calculated by the VIM equation of state along with the experimental data (Zagoruchenko and Zhuravlev, 1969). Equations 44 and 45 are used to predict C_v and C_p of methane, respectively. These computations, Figures 2 and 3, show a very good agreement with the experimental (Younglove, 1974) data.

Another test of an equation of state is its accuracy in predicting the critical properties P_c, ρ_c and T_c. Table 6 compares critical constants as calculated by the VIM equation of state with the experimental data (*CRC Handbook*, 1979) of argon and methane; agreement of predictions with the experimental data is quite satisfactory.

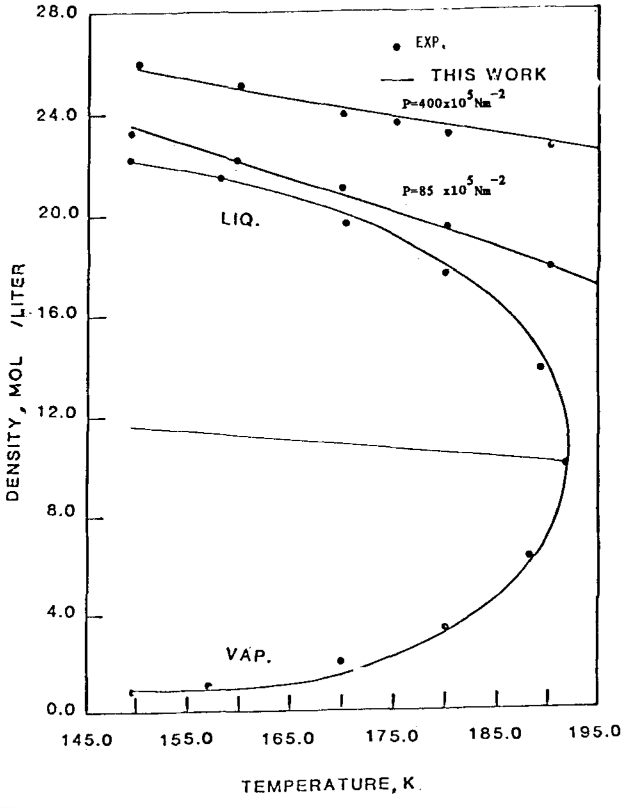

Figure 1. Saturation curve of methane as calculated by VIM equation of state and compared with experimental data (Zagoruchenko and Zhuravlev, 1969).

TABLE 6. CRITICAL CONSTANTS OF ARGON AND METHANE AS CALCULATED BY VIM EQUATION OF STATE AND COMPARED WITH EXPERIMENTAL DATA*

	Argon		Methane	
	VIM	exptl	VIM	exptl
T_c[K]	159.6	150.8	191.2	190.6
P_c[Nm^{-2}] × 10^5	48.13	48.74	48.23	46.0
V_c[cc/mol]	76.1	74.9	99.01	99.0

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* Experimental data is taken from *CRC Handbook* (1979).

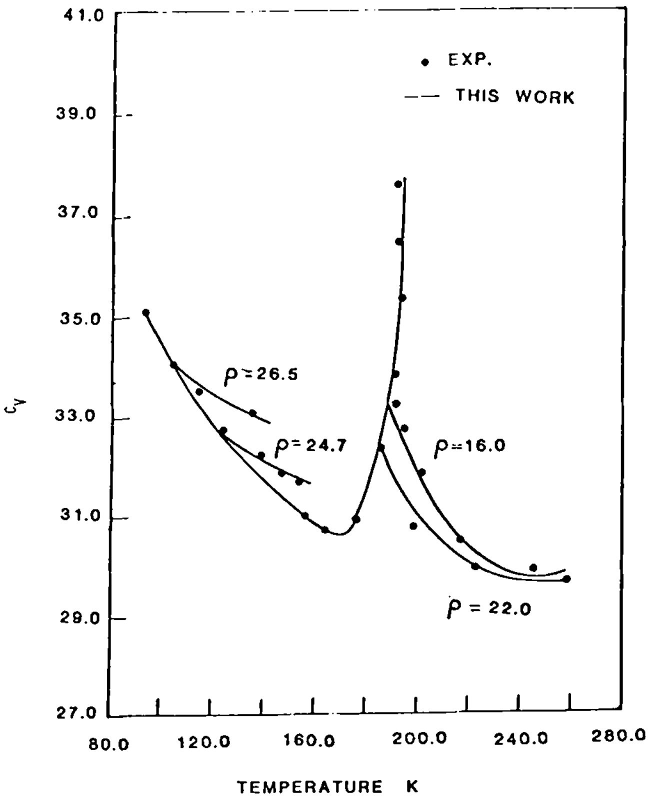

Figure 2. Heat capacity at constant volume C_v (J/K·mol) vs. temperature for methane at different densities ρ(mol/L) and in saturation region calculated by VIM theory, Eq. 44, and compared with experimental (Younglove, 1974) data.

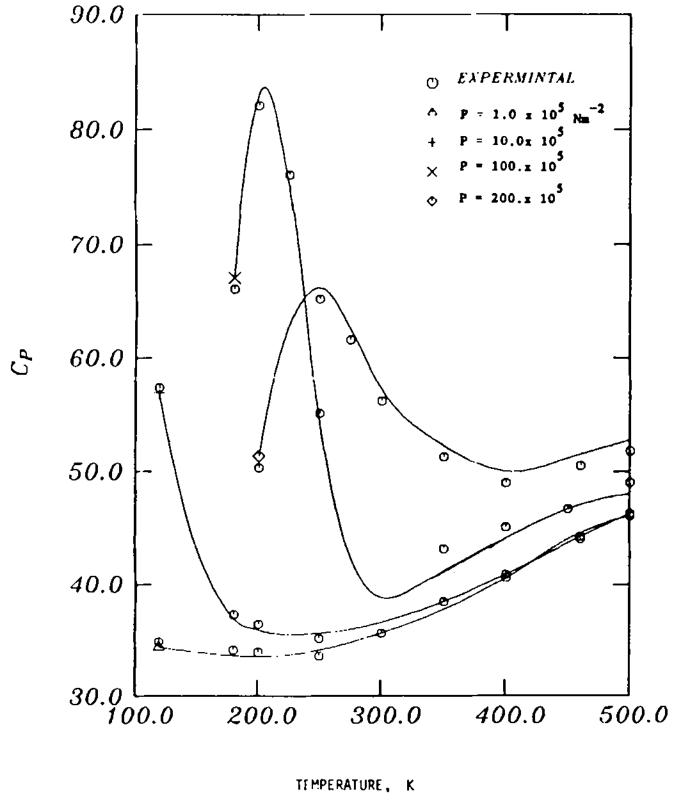

Figure 3. Heat capacity at constant pressure C_P(J/K·mol) vs. temperature [K] for methane at different pressures as compared with experimental data (Younglove, 1974).

According to the comparisons made with the experimental thermodynamic data, the VIM equations of state is an analytic equation of state based on the statistical mechanical grounds which can be used for accurate prediction of thermodynamic properties of nonpolar liquids and vapors. We have also applied the VIM theory to the case of polar fluids, quantum fields, and associated molecular fluids the results of which will be presented in subsequent publications.

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NOTATION

a_i = coefficients defined in Eq. 23
A = Helmholtz free energy
$c = d/\sigma$ = cut-off parameter
C_{nl} = coefficients defined in Eq. 28
C_p = heat capacity at constant pressure
C_v = heat capacity at constant volume
d = hard-sphere diameter
f_i = defined by Eqs. 30 and 31
g_{o2} = hard-sphere fluid pair-distribution function
g_{o3} = hard-sphere fluid triplet-distribution function
H = enthalpy
I_n = defined by Eq. 28
J_n = defined by Eq. 35
k = Boltzmann constant
N = number of molecules
N_a = Avogadro's number
P = pressure
PF = partition function
Q = configurational integral
r_{ij} = intermolecular distance
r_i = molecular position vector
R = universal gas content
S = entropy
T = absolute temperature
U = internal energy
V = volume
$x = r/d$ = dimensionless intermolecular distance
$Z = PV/NkT$ = compressibility factor

Greek Letters

α_i = coefficients defined in Eq. 41
λ = Lagrangian multiplier
ρ = molar density
$\underline{\phi}$ = total imtermolecular potential energy function
ϕ = pair intermolecular potential energy function
ψ_{ijk} = triplet intermolecular potential energy function
η = dimensionless density
σ = Lennard-Jones length parameter
ϵ = Lennard-Jones energy parameter
ν = Axilrod-Teller energy parameter
θ_i = angle between r_{ij} and r_{ik}

Subscripts

$2b$ = due to pair interactions
$3b$ = due to triplet interactions
c = critical property
int = due to internal degrees of freedom
o = hard-sphere reference fluid

Superscripts

con = configurational property
exptl = experimental property
ig = ideal gas property
$*$ = dimensionless property

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