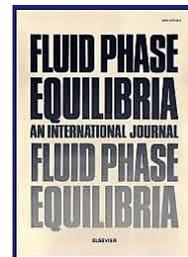# ANALITIC VIM EQUATION OF STATE

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ABSTRACT

Variational inequality minimization (VIM) theory of statistical mechanics is used to derive analytic equations of state for nonpolar and polar fluids. Thermodynamic properties of a variety of fluids in the liquid and vapor phases are predicted via the use of the VIM equation of state. The results of the predictions are shown to be in very good agreement with the experimental data for the majority of the fluids which are studied.

BACKGROUND AND THEORY

The following inequality holds between Helmholtz free energies of two thermodynamic systems with identical temperature, volume, and number of molecules but with different intermolecular potential energy functions

$$A_c \leq A_{oc} + \langle \underline{\phi} - \underline{\phi}_{oo} \rangle. \tag{1}$$

Inequality 1 is known as the Gibbs-Bogoliubov inequality [Mansoori and Canfield]. 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 non-simple system, we may minimize the right-hand side of this inequality in order to calculate the Helmholtz free energy and other thermodynamic properties of the non-simple system. In the present report we introduce a computational scheme, based on this inequality for the development of accurate, and algebraically analytic, equations of state of nonpolar and polar fluids. In the case when two-body ϕ and three-body ψ interaction potential energy functions are considered and with the use of the hard-sphere model of diameter d as the reference fluid and introduction of the concept of pair-and triplet-distribution functions of the hard-sphere reference, g_{o2}, g_{o3}, in inequality 1, we will derive the following inequality for the Helmholtz free energy

$$A \leq A_o + A_{2b} + A_{3b}, \tag{2}$$

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

$$A_{2b} = \iint g_{o2}(\underline{r}_{12}) \phi(\underline{r}_{12}) d\underline{r}_1 d\underline{r}_2$$

and

$$A_{3b} = \iiint g_{o3}(123) \Psi(123) d\underline{r}_1 d\underline{r}_2 d\underline{r}_3. \tag{4}$$

In order to utilize inequality 2 for calculation of the Helmholtz free energy, and other thermodynamic properties, of fluids its right-hand side should be minimized with respect to d according to the following conditions

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$$A' = (\partial A_o / \partial d)_{\rho,T} + (\partial A_{2b} / \partial d)_\rho + (\partial A_{3b} / \partial d)_\rho = 0, \tag{5}$$

$$A'' = (\partial^2 A_o / \partial d^2)_{\rho,T} + (\partial^2 A_{2b} / \rho d^2)_\rho + (\partial^2 A_{3b} / \partial d^2)_\rho > 0. \tag{6}$$

Eq.2 in conjunction with condition 5 is usually used to find a temperature-and density-dependent relation for the hard-sphere reference diameter [Mansoori and Canfield], $d = d(\rho,T)$, as the variational parameter. This procedure can be used for the accurate prediction of properties of simple fluids for which the potential energy functions are pairwize and close to a hard-sphere model and with exact knowledge about their potential energy parameters. For realistic fluids inequality 2, 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-upper-bound 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.

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

$$A_o = A^{ig} + RT\eta(4-3\eta)/(1-\eta)^2, \tag{7}$$

where, $\eta = \frac{\pi}{6}\rho N_o d^3$, is a dimensionless density and N_o is Avogadro's number. Provided we know the hard-sphere diameter which would give the minimum of the right-hand side of inequality 2, we could then write

$$A = A^{ig} + RT\eta(4-3\eta)/(1-\eta)^2 + A_{2b}(\rho,d) + A_{3b}(\rho,d) \tag{8}$$

From eq.8 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 in order to calculate thermodynamic properties. However, this is not necessary for the calculation of entropy. According to thermodynamics $S=-(\partial A/\partial T)_\rho$. Then according to eq.8 and with con-sideration of the variational condition 5 we conclude that

$$S(\rho,T) = S^{ig} - R\eta(4-3\eta)/(1-\eta)^2 = S_o(\eta) \tag{9}$$

According to this relation the entropy of a real fluid is equivalent to the entropy of a hard-sphere fluid provided that an appropriate temperature- and density-dependent hard-sphere diameter for the reference hard-sphere molecules is chosen which will satisfy variational conditions 5 and 6. Due to the simplicity of eq.9 it can be used to calculate η (or d) from the experimental entropy data of a fluid. Solving eq.9 for η results in the following expression

$$\eta = \frac{\pi}{6}\rho N_o d^3 = \{2 + (S-S^{ig})/R \pm 2[1+4(S-S^{ig})/R]^{1/2}\}/\{12 - (S-S^{ig})/R\}. \tag{10}$$

By applying entropy data of different fluids, eq.10 can be used to calculate the hard-sphere reference diameter d versus density and temperature. For all the varieties of fluids which are tested and for all the temperature and density ranges of the experimental entropy data, computation of the hard-sphere diameter indicates that it is linearly dependent on density and inversely dependent on temperature, for both the vapor and liquid phases. The hard-sphere diameter can be accurately correlated by

$$d(\rho,T) = a_o + a_1\rho + a_2/T + a_3\rho/T. \tag{11}$$

Numerical values of coefficients a_i for argon, methane, carbon dioxide, and methyl chloride are reported in Table 1. Due to the availability of this simple

and accurate relation for the hard-sphere reference diameter, one would not need to calculate this parameter from inequality 2. However, since this parameter accurately correlates the experimental entropy data, we can safely assume that it will minimize the right-hand side of inequality 2. 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 5 and 6 are satisfied. This can be accomplished by considering 5 and 6 as constraints in the calculation of the potential energy parameters of model potentials from the experimental PVT or any other experimental thermodymamic data. This will also alleviate the difficulty which is associated with the sparsity of inter-molecular potential parameter data which sometimes widely varies from one literature source to another.

ANALYTIC VIM EQUATION OF STATE OF POLAR FLUIDS

The intermolecular pair potential energy function of polar molecules may be represented by the Lennard-Jones function, together with the angle-averaged contributions of dipole, quadrupole, and dipole-quadrupole moment interactions, as originally introduced by Cook and Rowlinson.

$$<\phi(r_{12})>_\omega = 4\varepsilon[(\sigma/r_{12})^{12} - \frac{7}{20}(7Q^{*4}/T^*)(\sigma/r_{12})^{10}$$
$$- \frac{1}{4}(\mu^{*2}Q^{*2}/T^*)(\sigma/r_{12})^8 - \{1+\mu^{*4}/(12T^*)\}(\sigma/r_{12})^6] \qquad (12)$$

where $\mu^* = \mu/(\varepsilon^{1/2}\sigma^{3/2})$ and $Q^* = Q/(\varepsilon^{1/2}\sigma^{5/2})$. In these equations ε and σ are the energy and length parameters of the Lennard-Jones potential function, μ is the dipole moment and Q is the quadrupole moment. For the three-body potential function we use the Axilrod-Teller triple-dipole function

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

where ν is a constant. Substituting 12 and 13 into 2 and replacing the inequality sign by an equality sign, we derive the analytic expression for the Helmholtz free energy of a polar fluid

$$A/RT = A^{is}/RT + \eta(4-3\eta)/(1-\eta)^2 + \frac{48n}{T^*}[c^{-12}I_{12}(\eta) - \frac{7}{20}c^{-10}(Q^{*4}/T^*)I_{10}(\eta)$$
$$- \frac{1}{4}c^{-8}(\mu^{*2}Q^{*2}/T^*)I_8(\eta) - c^{-6}\{1+\mu^{*4}/(12T^*)\}I_6(\eta)] + \frac{\nu^*}{T}c^{-9}(f_1/f_2). \qquad (14)$$

By using the relationship between pressure and the Helmholtz free energy and application of condition 5, the following analytic expression for the compres-sibility factor of polar fluids may be derived

$$Z = P/\rho RT = (1+\eta+\eta^2-\eta^3)/(1-\eta)^3$$
$$+ \frac{48n}{T^*}[c^{-12}\{I_{12}(\eta)+J_{12}(\eta)\} - \frac{7}{20}c^{-10}(Q^{*4}/T^*)\{I_{10}(\eta)+J_{10}(\eta)\}$$
$$- \frac{1}{4}c^{-8}(\mu^{*2}Q^{*2}/T^*)\{I_8(\eta)+J_8(\eta)\} - c^{-6}\{1+\mu^{*4}/(12T^*)\}\{I_6(\eta)+J_6(\eta)\}]$$
$$+ \frac{\nu^*}{T^*c^9}(\frac{f_1'f_2-f_1f_2'}{f_2^2})$$

where $\nu^* = \frac{\nu}{\varepsilon\sigma^9}$ and

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

$$f_1 = 5.17184\eta + 6.16139\eta^2 - 2.19927\eta^3; \quad f_2 = 1 - 1.12789\eta + 0.73166\eta^2$$

$$f_1' = 5.17184 + 12.32278\eta - 6.59781\eta^2; \quad f_2' = -1.12789 + 1.46332\eta.$$

Supposing we know the potential energy parameters ε, σ, ν, the dipole and quadrupole moments μ, Q, and the hard-sphere diameter of a fluid. Eq.15 can then be used to calculate the pressure of a fluid at different temperatures and densities (this equation will be valid for nonpolar fluids when $\mu=Q=0$). However, the accuracy of PVT predictions by eq.15 is very sensitive to the values of the potential parameters. The potential energy parameters reported in the literature are rather sparse and inconsistent. In order to apply eq.15 for the accurate thermodynamic prediction of nonpolar and polar fluids, potential energy parameters should be recalculated according to the following procedure:

Parameters ε, σ, and ν appearing in eq.15 may be considered as three adjustable parameters for fitting the experimental compressibility data to eq.15. But, since these parameters should also be chosen such that conditions 5 and 6 will be satisfied, we will need to minimize

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

with the following constraints

$$\sum_{j=1}^{n} A_j' = 0; \qquad \sum_{j=1}^{n} A_j'' > 0. \tag{17}$$

where Z_j^{exptl} is the experimental compressibility, Z_j is the compressibility as calculated by eq.15. A_j' and A_j'' are given by 5 and 6, respectively, all for the jth data point, and n is the number of data points used. This minimization problem can be solved by introducing a Lagrangian multiplier λ such that

$$\sum_{j=1}^{n} (Z_j^{\text{exptl}} - Z_j)^2 + \lambda \sum_{j=1}^{n} A_j' = \text{minimum}, \tag{18}$$

with respect to ε, σ, and ν. With the choice of an appropriate set of experimental PVT data, minimization of eq.18 will produce the numerical values for the potential energy parameters. For polar molecules usually there are reliable dipole moment data available in the literature. However the quadrupole moment data for molecules are rather scarce and vary according to the source. Due to this problem eq.18 should be actually used for calculating ε, σ, ν, and Q. In Table 3 values of ε, σ, ν, and Q for a number of nonpolar and polar fluids are reported as calculated by the present technique along with the experimental dipole moment μ data.

In applying the VIM equation of state for calculating thermodynamic properties of polar fluids we will need to construct a dimensionless relationship for the reference hard-sphere diameter, eq.11, with respect to temperature and density:

$$c = \frac{d}{\sigma} = \alpha_0 + \alpha_1 \rho^* + \alpha_2/T^* + \alpha_3 \rho^*/T^* \tag{19}$$

where $T^* = kT/\varepsilon$, $\rho^* = N_0 \rho \sigma^3$. We then express $\alpha_i (i=0,1,2,3)$ as

$$\alpha_i = \alpha_{i0} + \alpha_{i1} \nu^* + \alpha_{i2} \mu^* + \alpha_{i3} Q^*, \qquad (i=0,1,2,3). \tag{20}$$

All the values of universal coefficients α_{ij} $(i,j=0,1,2,3)$ are calculated and are reported in Table 2. With the availability of these universal coefficients the VIM equation of state can be used for calculation of thermodynamic properties of other nonpolar and polar fluids provided that their potential energy parameters are already known. Thermodynamic properties of a number of nonpolar and polar fluids are calculated by the VIM equation of state and they are reported here. Accurate calculation of thermodynamic properties through the variational inequality minimization technique indicates that it is possible to produce algebraically analytic equations of state for nonpolar and polar fluids which are accurate and are based upon 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 these fluids in the critical region and away from the critical region in both the liquid and vapor phases. Comparisons of the results of the VIM equation of state with the experimental data indicate that by consideration of nonpolar, dipolar, quadrupolar and dipolar-quadrupolar interactions it is possible to derive equations of state which are accurate and simple enough to be used for engineering design calculations. Application of the VIM equation of state for the prediction of thermodynamic properties of argon, methane, carbon dioxide, methyl chloride, ethane, iso-butane, and sulphur dioxide and prediction of scaling law critical exponents has been successful. It is expected that the VIM equation of state will be equally successful for calculation of thermodynamic properties of other nonpolar and polar fluids. The availability of the VIM equation of state for polar and non-associated molecular fluids which is introduced in the present report is a prerequisite for its extension to the case of polar and associated molecular fluids.

ACKNOWLEDGMENT

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TABLE 1
Coefficients, of eq.11, the hard-sphere diameter, of argon, methane, carbon
dioxide, and methyl chloride with d in Å and ρ in mol/1.

	argon	methane	carbon dioxide	methyl chloride
a_0	3.1885	3.6999	3.2868	3.6951
a_1	-0.00811	-0.00641	0.01349	-0.18508
a_2	26.3250	24.5914	342.973	-1.69349
a_3	-0.5176	-0.8506	-10.757	5.1704
RMSD	0.003	0.013	0.016	0.026
entropy data	(i,ii)	(iii,iv)	(i,v)	(vi,vii)

(i) Vargaftik (1975) and Rowlinson, et.al (1980). (ii) Rowlinson, et.al
(1980). (iii) Hsu, et.al (1964). (iv) Rodgers, et.al (1974). (v) Din
(1961). (vi) Goodwin (1974). (vii) McDowell and Kruse (1963).

TABLE 2
Coefficients C_{ni} of polynomial 16 for different values of exponent n(6,8,10,12,14)

i	C_{6i}	C_{8i}	C_{10i}	C_{12i}	C
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

TABLE 3
Intermolecular potential energy parameters of a number of polar and nonpolar
molecules calculated through the VIM theory and the experimental dipole moment
data reported by Smyth (1955). In this table ε/k is in [K], σ is in
[Å], Q is in [$erg^{0.5}cm^{2.5}$], ν/k is in [Å^{9}K] and μ is in [$erg^{0.5}cm^{1.5}$].

substance	ε/k	σ	$Qx10^{26}$	$(\nu/k)x10^{-4}$	$\mu x10^{18}$
Argon	115.90	3.412	0.0	6.385	0.0
Methane	144.9	4.002	0.0	47.897	0.0
Carbon Dioxide	194.64	3.984	5.162	124.10	0.0
Methyl Chloride	389.40	4.730	1.202	103.633	1.8
Ethane	197.32	4.537	0.55	33.12	0.0
Hexane	401.65	7.301	2.35	43.29	0.0
Heptane	413.21	8.018	3.12	68.110	0.0
Iso-Butane	287.30	5.326	2.345	19.68	0.1
Sulphur Dioxide	352.37	4.102	4.12	87.631	1.7

TABLE 4
Universal coefficients a_{ij} of eq.20.

	j=0	j=1	j=2	j=3
i=0	0.958047	-2.666531	0.217005	-0.0661946
i=1	-0.236503	15.527093	-0.511675	-0.2453656
i=2	0.124900	-6.568512	-0.215738	0.4858472
i=3	-0.095197	4.553687	0.225446	-0.3861569

TABLE 5

Density and compressibility of methyl chloride, iso-butane, and sulphur dioxide as calculated by the VIM equation of state, eq.15, and compared with the experimental data

T [K]	P [bar]	ρ_{exptl} [mol/l]	ρ_{calc} [mol/l]	Z_{exptl}	Z_{calc}
METHYL CHLORIDE					
323.15	6.14	0.250	0.246	0.914	0.927
323.15	10.36	0.445	0.442	0.866	0.872
373.15	6.26	0.211	0.210	0.956	0.958
373.15	31.54	1.487	1.486	0.684	0.684
416.25	41.54	1.640	1.629	0.732	0.737
416.25	51.72	2.380	2.361	0.628	0.633
448.15	51.56	1.848	1.835	0.749	0.754
448.15	81.45	3.994	3.967	0.547	0.551
498.15	209.25	9.470	9.443	0.534	0.535
498.15	315.67	11.806	11.725	0.646	0.650
ISO-BUTANE					
313.15	40.0	8.866	9.311	0.173	0.165
393.15	40.0	6.886	6.836	0.178	0.179
313.15	80.0	9.490	9.483	0.324	0.324
393.15	80.0	7.353	7.530	0.333	0.325
313.15	120.0	10.003	9.622	0.461	0.479
393.15	120.0	7.453	7.929	0.493	0.463
293.15	160.0	9.940	10.130	0.660	0.648
393.15	160.0	7.999	8.199	0.612	0.597
293.15	200.0	10.464	10.219	0.784	0.803
353.15	200.0	9.451	9.168	0.721	0.743
SULPHUR DIOXIDE					
323.15	100.33	20.611	21.329	0.181	0.175
348.15	41.46	19.150	19.922	0.075	0.072
348.15	282.82	20.277	20.003	0.482	0.488
373.15	28.045	17.370	17.010	0.052	0.053
373.15	309.91	19.227	19.216	0.519	0.520
398.15	74.44	16.082	16.082	0.140	0.140
398.15	307.97	18.237	18.276	0.510	0.509
430.15	76.14	6.474	6.377	0.329	0.334
430.65	296.93	16.271	16.292	0.610	0.509
473.15	311.21	14.211	14.051	0.557	0.563

TABLE 6

Prediction of internal energy of ethane using the VIM equation of state and compared with the experimental data reported by Goodwin, et.al (1976).

T [K]	P [bar]	ρ_{exptl} [mol/l]	U_{exptl} [J/mol]	U_{calc} [J/mol]
100.0	60.0	21.404	5,928.9	6,026.3
240.0	60.0	15.854	15,939.9	16,173.6
100.0	100.0	21.454	5,898.8	5,996.2
240.0	100.0	16.101	15,767.4	16,001.1
100.0	200.0	21.573	5,827.5	5,924.9
240.0	200.0	16.607	15,415.4	15,649.1
100.0	300.0	21.687	5,761.3	5,858.7
250.0	300.0	16.657	15,843.3	16,086.7
100.0	400.0	21.796	5,699.6	5,797.0
250.0	400.0	17.028	15,589.4	15,832.8

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TABLE 7
Critical constants of a number of non-polar and polar fluids as calculated by
the VIM equation of state and compared with the experimental data

substance	T_c		P_c		V_c	
	VIM	exptl	VIM	exptl	VIM	exptl
Argon	159.6	150.8	47.5	48.1	76.1	74.9
Methane	191.2	190.6	47.6	45.4	99.0	99.0
Carbon Dioxide	304.9	304.2	75.3	72.8	92.6	94.0
Methyl Chloride	412.2	416.3	79.2	65.9	126.3	139.0
Ethane	309.8	305.4	47.6	48.2	146.8	148.0
Sulphur Dioxide	433.6	430.8	79.3	77.8	123.6	122.0

TABLE 8
Critical Exponents measured experimentally and calculated by different theories.

	α	β	γ	δ
exptl (a,b,c)	0.125±0.025	0.325±0.004	1.25±0.03	4.5
vdW equation (d)	0.0	0.5	1.0	3.0
Ising model (b)	0.110	0.325	1.24	4.82
mol. dyn. (a)	0.20±0.1	0.50±0.05	1.0±0.1	3.0±0.3
VIM theory	0.086	0.371	1.39	4.762

(a) Alder et al. (1972), (b) Sengers et al. (1977), (c) Green et al. (1967)
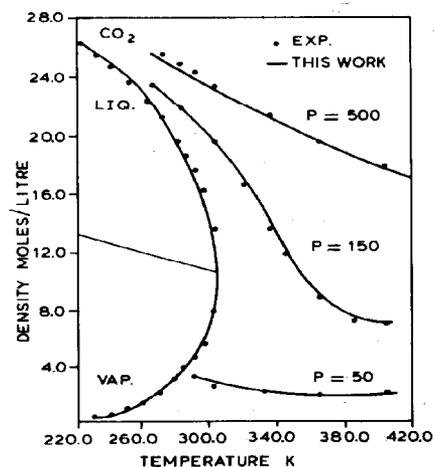(d) Levelt-Sengers (1970).

Figure 1: Isobaric saturation curve of carbon dioxide with different isobars at
50, 150, and 500 bars as calculated by the VIM equation of state and compared
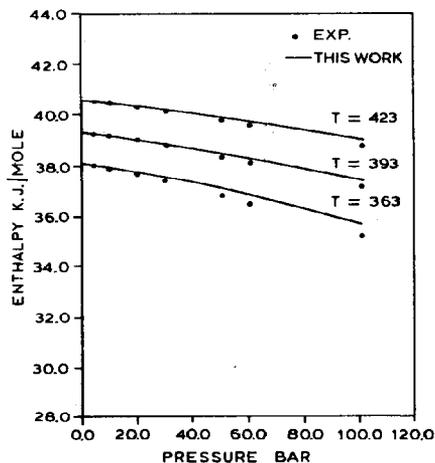with the experimental data reported by Rowlinson et al. (1980).

Figure 2: Enthalpy of carbon dioxide in the dense gas phase as calculated by
the VIM equation of state and compared with the experimental data reported by
Raznjevic at different temperatures.