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CHAPTER 16

ANALYTIC VARIATIONAL-YUKAWA EQUATION OF STATE

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Up to a few years ago, there was very little use of fundamental statistical thermodynamic theories in predicting thermodynamic properties of real fluids, particularly for liquids and phase transitions. This was mostly due to the complexity of the fundamental theories. Recent developments in statistical thermodynamics indicate that fundamental theories are capable of producing simple and accurate analytic relations for thermodynamic properties of liquids and vapors, and that more serious consideration must be given to these theories in predicting properties of fluids of industrial importance [1,2]. In this chapter, based on the variational theory of statistical thermodynamics and with the use of the Yukawa-type intermolecular potential energy functions, analytic equations of state are developed for fluids (vapors and liquids). The resulting equations of state are accurate enough to take the place of the existing empirical approaches of equation of state.

MULTI-YUKAWA POTENTIAL ENERGY FUNCTION

The pair-potential energy function between two molecules can, in principle, be represented by a multi-Yukawa potential energy function given by:

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$$u(r) = \infty \text{ for } r < \gamma$$

$$u(r) = \sum_i \frac{a_i}{b_i} \frac{e^{-b_i r}}{r} \text{ for } r > \gamma \quad (1)$$

where a_i and b_i are potential parameters and γ is the hardcore interaction diameter. The simplest form of the multi-Yukawa function that can be considered in representing the pair-potential energy function of two molecules in a two-Yukawa potential with one positive and one negative Yukawa tail is:

$$u(r) = \infty \text{ for } r < \gamma$$

$$u(r) = \frac{a_1}{b_1} \frac{e^{-b_1 r}}{r} - \frac{a_2}{b_2} \frac{e^{-b_2 r}}{r} \text{ for } r > \gamma \quad (2)$$

However, Equation 2 can be reformulated with respect to the known potential energy parameters ϵ and r_m in the form:

$$u(r) = \infty \text{ for } X < \gamma/r_m$$

$$u(r) = -\frac{\epsilon}{X} \frac{(1 + B_2)e^{-B_1(X-1)} - (1 + B_1)e^{-B_2(X-1)}}{(B_2 - B_1)} \text{ for } X > \gamma/r_m \quad (3)$$

where ϵ = minimum potential energy
 r_m = intermolecular distance at the minimum
 B_1, B_2 = parameters that should be specified for the interacting molecules

VARIATIONAL EQUATION OF STATE

According to the Gibbs-Bogoliubo inequality [2], the following inequality holds between the Helmholtz free energy of a real fluid and the Helmholtz free energy of a hard-sphere fluid [3]:

$$A \leq A^{hs}(d) + 2\Pi\rho NI(\rho N, d) \quad (4)$$

and

$$A^{hs}/NKT = A^{ig}/NKT + \frac{\eta(4-3\eta)}{(1-\eta)^2} \quad (5)$$

where ρ_N = number density
 N = number of molecules in the two systems (real fluid and hard-sphere fluid)
 η = the dimensionless density

Also,

$$\eta = \frac{\Pi}{6} \rho_N d^3 \quad (6)$$

and $I(\rho_N, d)$ is given by:

$$I(\rho_N, d) = \int_d^{\infty} g_{hs}(r, d) u(r) r^2 dr \quad (7)$$

where g_{hs} = hard-sphere radial distribution function
 d = hard-sphere molecular diameter.

To bring the inequality of Equation (4) closer to equality, we need to minimize its right-hand side with respect to the reference hard-sphere fluid diameter d , i.e.,

$$\left(\frac{\partial A^{hs}}{\partial d} \right)_{\rho, T} + 2\Pi\rho_N N \left(\frac{\partial I(\rho, d)}{\partial d} \right)_{\rho} = 0 \quad (8)$$

Equation 8 is the condition that should hold if we are to replace the inequality relation (Equation 4) with an equation like:

$$A = A^{hs}(\eta, T) + 2\Pi\rho_N I(\rho_N, d) \quad (9)$$

With the use of Equations 8 and 9, we can derive relations for other thermodynamic properties of fluids. For example, it can be shown that compressibility is in the following form:

$$Z = \frac{PV}{NKT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} + \frac{2\Pi\rho}{kT} \left(1 + \eta \frac{\partial I}{\partial \eta} \right)_{d, T} \quad (10)$$

An interesting feature of the variational equation of state is its relation for entropy, which reduces to the hard-sphere entropy, i.e.,

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$$S/NK = S_{ig}/NK - \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \quad (11)$$

According to this equation, the entropy of a real fluid can be represented by entropy of a hard-sphere fluid, provided a proper temperature and density-dependent relation for the hard-sphere diameter is available. With the availability of the relations for A, Z and S, other thermodynamic properties of the fluid can be calculated.

By inserting Equation 3 into Equation 7 and by using the analytic solution of the hard-sphere radial distribution function according to the Percus-Yenick theory [1,2], we get the following analytic relation for Helmholtz free energy:

$$\frac{A}{NkT} = \frac{A^{hs}}{NkT} + \frac{12\eta}{\xi T^*} \sum_{i=1}^2 (-1)^i A_i e^{+B_i G(B_i \xi)} \quad (12)$$

such that

$$G(B_i \xi) = \frac{L_i B_i \xi}{12\eta[L_i + S_i e^{B_i \xi}]} \quad (13)$$

$$L_i = 12\eta \left(1 + \frac{1}{2}\eta\right) B_i \xi + (1 + 2\eta) \quad (14)$$

$$S_i = (1 - \eta)^2 (B_i \xi)^3 + 6\eta(1 - \eta)(B_i \xi)^2 + 18\eta^2 B_i \xi - 12\eta(1 + 2\eta) \quad (15)$$

$$T^* = kT/e \quad (16)$$

$$\xi = d/r_m \quad (17)$$

From the above analytic equations of state, other thermodynamic properties of the fluid can be derived. However, the relation for entropy is still going to be the same as Equation 11.

APPLICATION OF THE EQUATION OF STATE FOR METHANE

To apply the equation of state for a real fluid it is necessary, first, to find the relationship for the hard-sphere diameter as a function of temperature and density. This can be done by using the relation for entropy (Equation 11),

and fitting it to the entropy data of a fluid. We have derived the following relation for methane using a wide range of experimental data [4]:

$$\xi = 0.921268 + \frac{0.033322}{T^*} - 1.536858 \times 10^{-8} \rho^* - 1.048225 \times 10^{-8} \frac{\rho^*}{T^*} \quad (18)$$

where $\rho^* = \rho r_{\min}^3$

This relation for ξ holds for methane in both liquid and vapor phases. Also, the following potential energy parameters are derived for methane:

- $\epsilon/k = 185.45^\circ\text{K}$;
- $B_1 = 2.500 [-]$;
- $B_2 = 28.301 [-]$; and
- $r_m = 3.870 \text{ \AA}$.

With the use of Equation 10 for compressibility and the relation of ξ as given by Equation 18, compressibility of methane is calculated and reported in Table I for various temperatures and pressures in liquid phase. Also reported in this table are the experimental compressibility data together with the percentage error of each data point. As it is shown, predictions by Equation 10 are quite satisfactory. In all of the experimental methane data that were used, we got an average error of 1.93% and a maximum error of 3.73%. Predictions of the compressibility of the vapor phase are excellent, and they are not reported in the table. However, in Figures 1 and 2, several predicted isotherms and isobars of methane are reported and are compared with the experimental data in liquid and vapor phases.

Table I. Calculations of Compressibility Factors Using Equation 10: "Liquid Region"

T (°K)	P (bar)	Z _{exp}	Z (Equation 10)	% Error
121.16	64.484	0.247	0.2384	3.482
134.136	76.278	0.276	0.2725	1.268
147.448	130.424	0.446	0.434	2.710
148.828	44.459	0.157	0.1544	1.338
162.20	96.526	0.324	0.336	-3.731
166.497	130.432	0.427	0.4324	-1.453
171.921	116.374	0.383	0.3916	-1.484
172.603	40.302	0.144	0.1398	2.917
175.122	272.905	0.821	0.7946	3.22
181.163	90.419	0.308	0.3058	0.755
190.68	140.564	0.456	0.4606	-1.009
191.734	254.462	0.752	0.7442	1.085
193.924	83.993	0.306	0.2997	2.089

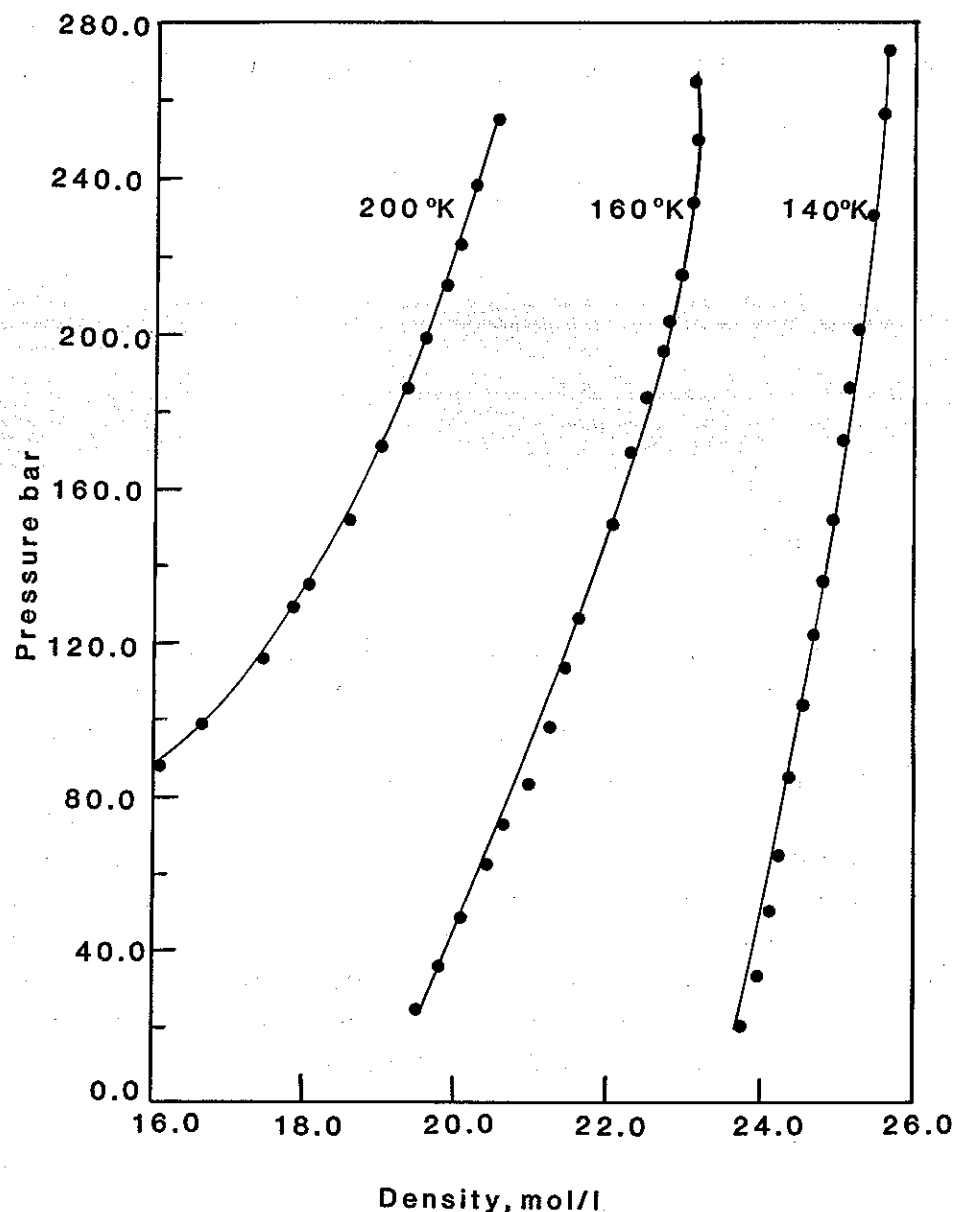


Figure 1. Pressure vs density for methane at different isotherms (— = this work; ● = Vargaftik [6]).

A severe test of an equation of state is its applicability for predictions of compressibility and heat capacities. The analytic variational-Yukawa equation of state for methane is also used for prediction of constant-volume heat capacity of liquid methane, and the results are reported in Table II. Knowing the simplicity of this equation of state, predicted results for heat capacity are in good agreement with the experimental data, with a maximum error of 9.5% and an average error of 2.7%. The predictions of the present equation of state are not as good as National Bureau of Standards empirical correlation [4] for heat capacity.

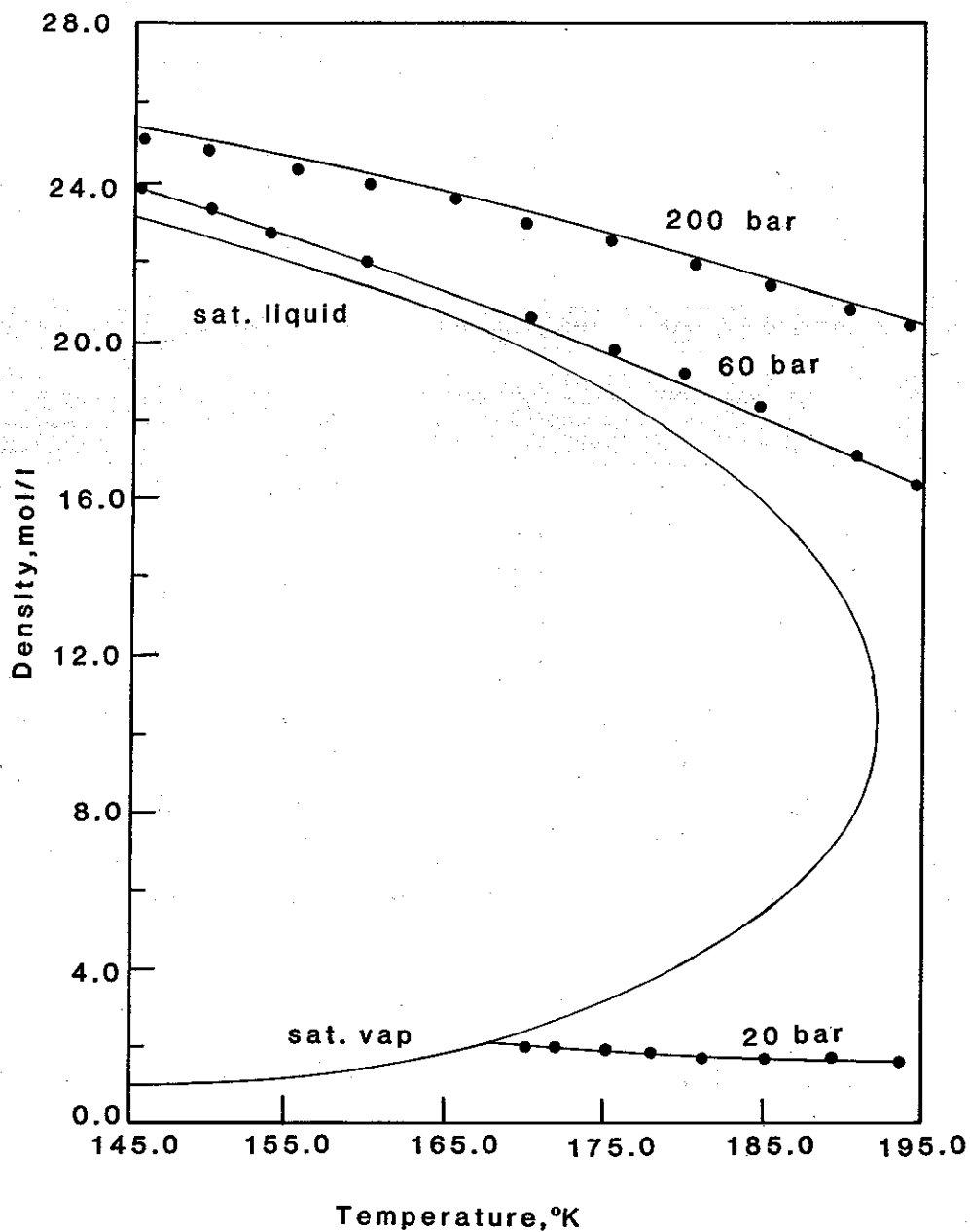


Figure 2. Density vs temperature for methane at different isobars (— = this work; ● = Vargaftik [6]).

CONCLUSIONS

The analytic variational-Yukawa equation of state has been shown to be successful for prediction of thermodynamic properties of methane in liquid and vapor phases. One of the features of this equation of state is its versatility in prediction of varieties of thermodynamic properties in both liquid and vapor phases. Successful application of this equation of state for methane

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Table II. Calculations of C_V Using Yukawa Potential Equation of State^a

T (°K)	P (bar)	ρ (mol/l)	C_V (J/mol-°K)		C_V	% Error
			Predicted	Experimental		
130.508	34.766	24.785	29.957	32.612	31.993	-9.08
147.448	130.924	23.972	29.916	31.612	32.213	-5.97
148.828	44.459	22.933	30.687	31.314	31.459	-2.00
153.984	30.864	22.126	31.684	31.04	31.271	2.03
162.80	96.526	22.098	30.494	30.80	30.966	-1.00
166.497	130.432	22.083	30.427	30.832	30.544	-1.33
171.921	116.374	21.278	31.147	30.496	29.683	2.13
172.603	40.302	19.50	32.441	30.637	29.445	7.52
178.581	37.972	18.086	34.007	31.28	30.072	8.72
181.643	90.419	19.479	31.561	30.306	29.476	3.97
184.764	45.449	16.723	34.817	31.727	30.621	3.61
187.325	58.459	17.007	33.384	31.221	30.119	6.93
187.949	51.074	16.103	35.086	32.04	30.863	9.51
189.591	55.934	16.032	35.031	32.832	30.727	6.70
190.68	140.564	19.547	31.241	30.082	29.317	3.71
191.734	254.462	21.217	28.893	30.126	29.536	-4.25
191.539	52.228	14.388	36.138	34.042	32.384	5.12
193.924	83.993	16.997	33.004	30.513	29.705	8.164
204.379	154.828	18.032	30.880	29.958	29.119	3.078
210.401	140.788	16.681	31.534	29.882	29.25	5.53
270.623	333.417	15.971	29.464	29.851	29.379	1.507

^aRoot mean square deviation = 0.191 for present work; 0.116 for Goodwin [3].

^bFrom Younglove [5].

has motivated us to apply it to a variety of fluids of interest in industry. Work on this subject is in progress.

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