

Comparison between four equations of state in predicting the temperature and density dependencies of the parameters of the average effective pair potential for dense methane

M. Souri

Payame Noor University, Iran

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In this work, four equations of state, namely MSRK, RK, Jan-Tsai and Nasrifar-Jalali were compared in predicting the parameters of the average effective pair potential for dense methane at various temperatures and densities. All equations of state show temperature and density dependencies for ε/k and σ : σ increases with temperature and ε decreases, while σ increases and ε decreases as density decreases.

Key Words: Average effective pair potential; Lennard-Jones potential; Equation of state

1. INTRODUCTION

Methane represents the most spherical molecule. The phase diagram of condensed methane is experimentally well investigated and exhibits a disordered phase upon solidification [1,2].

In statistical mechanics, the light and small methane molecule plays a key role. Its liquid phase represents the natural choice for investigating orientational effects upon spatial structural ordering and for examining the complex dynamic problem of translational - rotational coupling. Also, as the first representative of the homologous series of saturated hydrocarbons, the CH_4 molecule has vital importance for the description of the systematic changes in experimental physical and chemical properties with increasing number of CH_2 increments in alkanes and in relating these changes to particular molecular characteristics. Thus, it is not surprising that a huge number of potential models have been developed for modeling the liquid phase of methane [3].

The Lennard-Jones potential is:

$$u(r) = \frac{n\varepsilon}{n-m} \left(\frac{n}{m}\right)^{\frac{m}{n-m}} \left\{ \left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m \right\} \quad (1)$$

where σ is the separation at which the potential is zero, ε is the depth of the potential well and n and m are integers.

Lennard-Jones potential is a qualitative realistic

potential and is the most frequently used potential for gaseous and liquid systems even at dense fluid conditions. It is a simple pair potential function that possesses both repulsive and attractive London forces and has been extensively used owing to its simplicity [4,5].

Our aim in this work was to predict the temperature and density dependency of the Lennard-Jones potential, as an Average Effective Pair Potential (AEPP). Parsafar *et al.* [6] studied the density and temperature dependency of the Lennard-Jones parameters of dense fluids using linear isotherm regularity (LIR). Nasehzade and Azizi [7] introduced a new simple method to estimate the Lennard-Jones parameters for rare gases and n -alkanes at any desired temperature range from triple point to boiling point. Their approach was based on experimental data for the heat of vaporization, free energy of solution, as well as on the application of the scaled-particle theory (SPT) and other new expressions that give the free energy of cavity formation ΔG_c , in hard sphere fluids [8,9].

The state dependency of the Effective Pair Potential (EPP) parameters, the well depth, ε , and the intermolecular separation at constant σ , have been previously studied by some investigators *via* radial distribution function calculations and shape factor theory [10,11].

The interaction potential of an isolated pair is different from that of the pair in the presence of other molecules. This difference can be attributed to the effect of the medium on the molecular charge

* To whom all correspondence should be sent:

E-mail: msouri@pnu.ac.ir

distribution. In the absence of such an effect, the interaction potential of two isolated molecules depends on their intermolecular separation (for simple spherical molecules). However, this effect is important in dense fluids. Based on this idea, the concept of the EPP, which includes the effects of the medium plus the isolated pair interaction potential, was introduced. Such a potential is considered to be the interaction of two nearest neighbor molecules in which all of their longer-range interactions are added to it. Since the effect of a fluid medium on the electronic distribution of molecules is included, the total potential energy of the fluid can be represented exactly as the sum of all average effective pair interaction energies. Therefore, the pairwise additivity of the potential energy in terms of the AEPP is an exact treatment (if one can include all long-range potentials in AEPP) and the total potential energy of a fluid can be written as:

$$U = N/2 \bar{uz} \quad (2)$$

where \bar{u} is the AEPP, N is the number of molecules, and z is the average coordination number [6].

2. THEORY

In this work, four equations of state were compared in predicting temperature and density dependency of Lennard- Jones parameters.

The Redlich- Kwong equation of state is:

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \quad (3)$$

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} \quad b = \frac{0.08664RT_c}{P_c}$$

where P , T , V and R are pressure, temperature, volume and gas constant, respectively (see [12]). a and b are parameters of the equation of state T_c and P_c are the critical parameters of methane:

$$T_c = 190.564K \quad \text{and} \quad P_c = 4.59 \times 10^6 Pa$$

U , internal energy, can be derived from each equation of state by the following steps:

$$i) P_{th} = T \left(\frac{\partial P}{\partial T} \right)_V$$

$$ii) P_{in} = P_{tot} - P_{th}$$

$$iii) P_{in} = - \left(\frac{\partial U}{\partial V} \right)_T$$

where P_{th} is the thermal pressure and P_{in} is the internal pressure.

For Redlich- Kwong equation of state, the expression for the internal energy has the form:

$$U = \frac{1.5a}{b\sqrt{T}} \left(-\frac{b}{V} + \frac{b^2}{V^2} - \frac{b^3}{V^3} + \dots \right) \quad (4)$$

or:

$$U = \frac{1.5a}{b\sqrt{T}} (-b\rho + b^2\rho^2 - b^3\rho^3 + \dots)$$

On the other hand, using the (9,3) Lennard-Jones potential function as an EPP and applying eq. (2), the internal energy will be:

$$U = 1.299R(\varepsilon/k)Z(T, \rho)(\sigma^9\rho^3 - \sigma^3\rho) + 3RT \quad (5)$$

where the first term is the configurational energy and the second one is the kinetic energy of the fluid.

One can assume that:

$$Z(T, \rho) = A(T) + B(T)\rho \quad (6)$$

This is a simple function for the coordination number.

Inserting eq. (6) in eq. (5) and comparing the expression obtained for the internal energy with eq. (4) yields:

$$\sigma = \left(b^3 \frac{A}{B} \right)^{\frac{1}{6}} \quad (7)$$

and

$$\varepsilon/k = \frac{1.5a}{1.299RA\sigma^3\sqrt{T_c}} \quad (8)$$

Inserting eq. (7) and eq. (8) in eq. (5):

$$\left(\frac{(U - 3RT)\sqrt{T_c}}{1.5a\rho} - b^3\rho^3 + 1 \right) \Big/ \rho = \frac{A}{B} b^3\rho - \frac{B}{A} \quad (9)$$

The solution of eq. (9) provides a value of A/B for any values of U , ρ and T . Therefore σ can be obtained at any condition.

An expression for U can be derived from each equation of state that is listed in the Appendix. (Eq. 4 is an expression for the internal energy derived from Redlich- Kwong equation of state. Similar

derivation could be done for each equation of state in the Appendix). Comparing these expressions with eq. (5) using the method discussed above, permits to calculate σ values for each data point. The results of such calculations are summarized in Table 1.

The temperature dependency of σ for the RK EoS is shown in Figure 1. At any constant temperature σ decreases with density, but at higher temperatures the slope of variation is greater. In addition, at high densities the temperature dependency of σ is negligible and its values obtained at different temperatures are similar.

The other EoS exhibit analogous trends.

Figure 2 shows the density dependency of σ obtained from different equations of state at constant temperature, 400 K. As is shown, σ decreases with density at constant temperature. Although different equations of state do not predict the same value for σ at constant density, still within the range of data the profiles of Jan-Tsai, Nasrifar-Jalali and MSRK equations of state are parallel. In addition, σ values obtained from RK and MSRK equations of state show a considerable agreement with each other. Since the MSRK is a modified form of RK EoS, such similarity was expected.

One can observe a similar trend at any constant temperature.

One can write eq. (5) as follows:

$$U - 3RT = 1.299R \varepsilon/k A \left(1 + \frac{B}{A} \rho\right) (\sigma^9 \rho^3 - \sigma^3 \rho) \quad (9)$$

where ε/k and A are unknown. Therefore:

$$y = \frac{U - 3RT}{1.299R \left(1 + \frac{B}{A} \rho\right) (\sigma^9 \rho^3 - \sigma^3 \rho)} \quad (10)$$

where

$$y = A \varepsilon/k \quad \text{or} \quad \ln y = \ln A + \ln \varepsilon/k$$

Assuming that A is a function of T , such as $A = e^{\frac{\beta}{T}}$, one also has:

$$\ln y = \ln \varepsilon/k + \beta/T \quad (11)$$

$\ln y$ in terms of $1/T$ is not a straight line. Therefore ε/k is not a constant value. We suggest the following equation for y :

$$\ln y = a \ln(\rho/T) + b (\ln(\rho/T))^2 + \beta/T \quad (12)$$

Table 1. Parameter σ , calculated for methane at given conditions. (The experimental data for the internal energy of methane are taken from Ref. [13])

$\sigma/\text{\AA}$				U	ρ	T/K
Nasrifar- Jalali	Jan- Tsai	MSRK	R-K	(Jmol ⁻¹)	(molLit ⁻¹)	
6.65	5.25	5.28	5.29	14830	12.00	580
6.25	4.96	4.96	4.96	14500	13.69	580
5.97	4.77	4.74	4.74	14240	15.09	580
6.42	5.10	5.10	5.09	13880	12.36	560
6.05	4.85	4.80	4.79	13560	14.05	560
5.79	4.86	4.60	4.59	13290	15.46	560
6.20	4.98	4.92	4.91	12960	12.74	540
5.85	4.76	4.65	4.63	12620	14.44	540
5.62	4.61	4.47	4.45	12360	15.85	540
5.97	4.87	4.75	4.72	12040	13.14	520
5.65	4.67	4.51	4.48	11700	14.85	520
5.43	4.54	4.36	4.32	11440	16.25	520
5.75	4.77	4.60	4.55	11140	13.58	500
5.45	4.60	4.39	4.34	10800	15.29	500
5.25	4.48	4.26	4.21	10530	16.63	500
5.10	4.39	4.16	3.12	10320	17.85	500
5.01	4.35	4.11	4.06	10140	18.35	500
4.90	4.26	4.03	3.99	9995	19.74	500
3.95	4.21	3.99	3.95	9872	205.2	500
5.13	4.70	4.36	4.24	7615	12.68	400
4.92	4.59	4.23	4.12	7305	14.09	400
4.64	4.43	4.08	3.99	6837	16.25	400
4.45	4.35	3.99	3.91	6497	17.37	400
4.37	4.24	3.92	3.85	6238	19.16	400
4.30	4.18	3.88	3.81	6032	20.24	400
4.24	4.13	3.84	3.78	5866	21.16	400
4.20	4.09	3.81	3.76	5730	21.97	400
4.17	4.05	3.79	3.74	5616	22.68	360
4.85	4.69	4.31	4.17	6349	12.42	360
4.61	4.56	4.17	4.05	5955	14.15	360
4.45	4.46	4.08	3.98	5617	15.52	360
4.26	4.32	3.97	3.89	5191	17.59	360
4.45	4.45	4.07	3.97	3806	13.17	300
4.34	4.60	3.20	4.08	4323	14.38	300
4.23	4.52	4.12	4.02	4039	15.38	300
4.03	4.35	3.99	3.90	3442	16.94	300
3.96	4.28	3.93	3.86	3165	18.14	300
3.86	4.18	3.86	3.80	2760	19.93	300
3.81	4.11	3.81	3.75	2472	21.27	300
3.77	4.05	3.77	3.72	2253	22.33	300
3.75	4.01	3.75	3.70	2081	23.22	300
3.91	4.29	3.95	3.89	2027	17.89	260
3.80	4.16	3.85	3.80	1485	20.19	260
3.67	4.10	3.80	3.76	1137	21.27	260
3.71	4.03	3.76	3.72	886.5	22.87	260
3.69	3.98	3.73	3.69	695	23.80	260
4.07	4.37	4.02	3.99	568.6	16.60	200
3.95	4.20	3.89	3.87	-147.4	19.59	200
3.89	4.12	3.83	3.81	-509	21.06	200

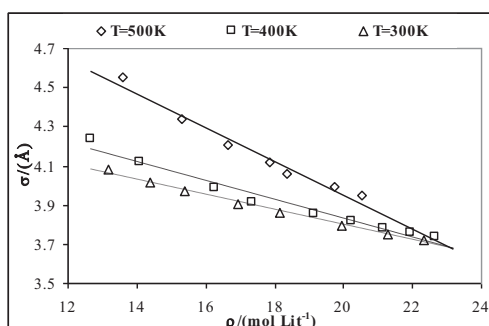


Fig. 1. Parameter σ in terms of density for RK equation of state at different temperatures.

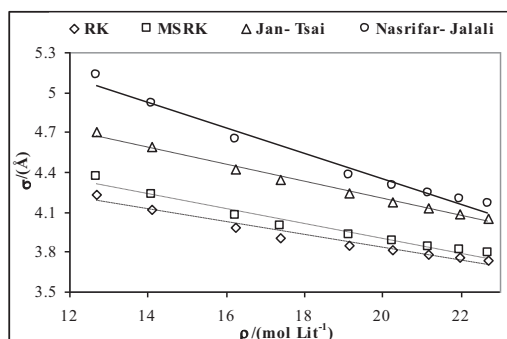


Fig. 2. Parameter σ vs density for different equations of state at constant temperature 400K.

This equation shows that ϵ/k is a function of temperature and density. Fitting of about 120 data points in eq. (12) with SIGMAPLOT software gave α , b and β with a negligible standard error. The parameters α , b and β and the relative standard errors for each equation of state are summarized in Table 2.

Eq. (12) indicated that:

$$\ln \epsilon/k = a \ln(\rho/T) + b(\ln(\rho/T))^2 \quad (13)$$

Therefore ϵ/k can be calculated for each temperature and density. The results of such calculations for each EoS are shown in Table 3.

Table 2. Fitting results for different equation of states

	RK		MSRK		Jan- Tsai	
	value	St. err.	value	St. err.	value	St. err.
α	-4.313	0.0893	-4.425	0.09446	-5.970	0.2401
b	-0.7875	0.02266	-0.8109	0.02396	-1.225	0.06089
β	246.8	20.87	225.8	22.06	74.05	56.07

Figure 3 shows the temperature dependency of ϵ/k for the RK EoS. This plot suggests that as the temperature increases, ϵ/k decreases. Such dependency can be observed for the other EoSs as well.

Figure 4 shows the density dependency of ϵ/k obtained from different EoSs at constant

temperature $T = 500$ K. For all EoSs examined ϵ/k increases with density. As can be seen, the ϵ/k values, obtained with the RK and MSRK EoSs are close together. Similar trend is observed at other constant temperatures.

Table 3. Parameter ϵ/k , calculated for methane at given conditions

	ϵ/k		U (Jmol ⁻¹)	ρ (mol L ⁻¹)	T (K)
	Jan-Tsai	MSRK			
136.82	15183	136.20	14830	12.00	580
231.74	18359	165.33	14500	13.69	580
329.06	21024	189.85	14240	15.09	580
178.52	17158	153.01	13880	12.36	560
282.27	204.85	183.47	13560	14.05	560
388.01	232.95	209.28	13290	15.46	560
224.84	192.95	171.58	12960	12.74	540
338.93	228.37	204.05	12620	14.44	540
450.55	256.55	229.81	12360	15.85	540
276.80	216.66	192.77	12040	13.14	520
399.06	252.83	225.86	11700	14.85	520
516.25	280.65	251.10	11440	16.25	520
333.04	241.65	215.58	11140	13.58	500
462.63	277.46	248.09	10800	15.29	500
582.36	304.26	272.18	10530	16.63	500
702.98	325.84	291.18	10320	17.85	500
765.27	338.53	302.87	10140	18.35	500
920.08	357.43	318.74	9995	19.74	500
1020.1	369.46	329.11	9872	20.52	500
392.71	267.20	239.30	10250	14.04	480
528.73	301.55	269.97	9911	15.74	480
683.57	329.98	294.46	9643	17.43	480
779.45	347.26	309.81	9428	18.27	480
303.00	244.38	219.55	9844	12.34	460
455.42	291.78	262.11	9381	14.54	460
598.93	324.35	290.52	9036	16.23	460
733.63	348.23	310.90	8769	17.60	460
859.35	366.64	326.38	8556	18.74	460

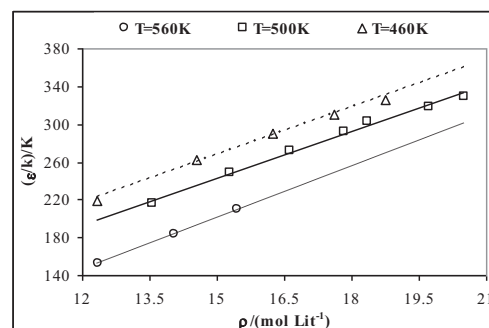


Fig. 3. Search for density dependency of the ϵ/k resulting from RK equation of state at different temperatures.

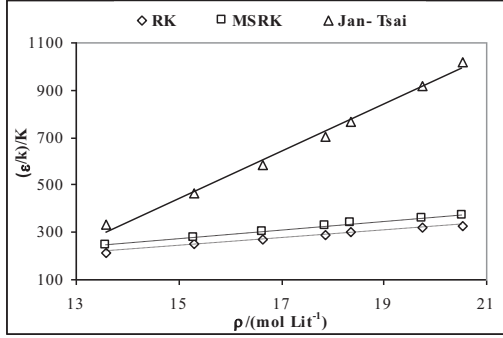


Fig. 4. Parameter ε/k in terms of density for various equations of state at constant temperature 500K.

3. CONCLUSION

Parsafar *et al.* [6] have shown that the parameters of the AEPP, σ and ε , are independent of density. Application of the CWA-VM theory (Chandler-Week-Andersen perturbation theory [14-17], analytically modified by the Verlet and Weis theory [18-19]) indicated that the obtained values of Lennard-Jones pair potential parameters are not constant and are dependent on temperature, so that when the temperature increases, σ increases and ε/k decreases [20].

As demonstrated above, σ and ε/k are dependent on temperature for all EoSs discussed.

Furthermore, the value of σ increases with temperature, while ε/k decreases. This is in agreement with previously reported results. When the parameter σ increases the repulsive branch of the potential shifts toward the longer separations. Therefore we may expect that as T increases, the potential well ε , decreases [6].

Potential parameters show density dependency: increasing density causes a decrease in σ values and an increase in ε/k . The reason behind this is the compression of the dense phase and the low free space between molecules. When density increases, molecules will pack closer together and σ decreases, which in its turn causes the shift in the repulsive branch of the potential toward shorter separations and the increase in ε/k values.

APPENDIX: The equations of state used

A1. Redlich- Kwong equation of state [12]

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)}$$

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} \quad b = \frac{0.08664RT_c}{P_c}$$

A2. Jan-Tsai equation of state [21]:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2}$$

$$\alpha = [1 + m_1 \ln(T_r)]^2$$

$$\alpha' = \frac{2m_1}{T} [1 + m_1 \ln(T_r)]$$

$$m_1 = -0.3936 - 0.6353\omega + 0.1132\omega^2 + 0.07673/Z_c$$

$$a = a_c \alpha$$

$$a' = a_c \alpha'$$

$$a_c = \frac{\Omega_a R^2 T_c^2}{P_c}$$

$$b = \frac{\Omega_b RT_c}{P_c}$$

$$\Omega_b = \frac{1 - 3\xi_c}{u - 1}$$

$$\Omega_a = 3\xi_c^2 + (u - w)\Omega_b^2 + u\Omega_b$$

$$\xi_c = 0.0889 + 0.750Z_c$$

$$u = \frac{2.277}{Z_c} - 5.975$$

$$w = -u(\Omega_b + 1) - \xi_c^2 \frac{3 - \xi_c/\Omega_b}{\Omega_b}$$

A3. MSRK (modified Soave Redlich- Kwong) equation of state [22]:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)}$$

$$a_c = 0.4286 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$a = a_c \alpha(T_r)$$

$$\alpha(T_r) = [1 + C_1(1 - \sqrt{T_r}) + C_2(1 - \sqrt{T_r})^2 + C_3(1 - \sqrt{T_r})^3]^2 \quad \text{for } T_r \leq 1$$

$$\alpha(T_r) = [1 + C_1(1 - \sqrt{T_r})]^2 \quad \text{for } T_r > 1$$

A4. Nasrifar-Jalali equation of state [23]:

$$Z = 1 + \frac{a_1 \xi + a_2 \xi^2}{(1 - \xi)^2} - \frac{(Z_m - 2)\xi \Gamma}{1 + \xi \Gamma}$$

$$Z_m = \frac{1}{3} (4\sqrt{2}\pi) R^3 - 1$$

$$\xi = \frac{V_0}{V} \quad V_0 = N_A \sigma^3 / \sqrt{2}$$

$$\Gamma = \exp(\varepsilon/kT) - 1$$

For methane: R=2,

$$\sigma = 3.487 \times 10^{-10} \text{ m}; \quad \varepsilon/k = 62.589 \text{ K.}$$

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СРАВНЕНИЕ МЕЖДУ ЧЕТИРИ УРАВНЕНИЯ НА СЪСТОЯНИЕТО ЗА ПРЕДСКАЗВАНЕ НА ЗАВИСИМОСТИТЕ НА ПАРАМЕТРИТЕ НА СРЕДНИТЕ ЕФЕКТИВНИ ПОТЕНЦИАЛИ НА МЕТАН ОТ ТЕМПЕРАТУРАТА И ПЛЪТНОСТТА

М. Сури

Университет "Паяме Нур", Иран

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(Резюме)

В тази работа са сравнени четири уравнения на състоянието (MSRK, RK, Jan-Tsai and Nasrifar-Jalali) при предсказване на осреднени ефективни потенциали (ϵ/k и σ) на метан при различни стойности на температура и плътност. Всички уравнения на състоянието, показват, че съществува зависимост между температура и потенциалите и между плътност ϵ/k и σ , както следва: с увеличаване на температурата σ се увеличава и ϵ намалява, докато при намаляване на плътността σ се увеличава, а ϵ намалява.