

A comparative study between the effective pair potential parameters obtained from different equations of states

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Internal energy of liquid methane has been obtained based on the pair-wise additive approximation for the effective pair potential of dense fluids using (12,6) Lennard-Jones model for the intermolecular potential function. This internal energy has been compared with the internal pressure via the equation of state (EoS) expression. Thus, the effective pair potential parameters (EPPP) through some given EoSs for dense fluids have been calculated. A relation between the potential parameters with EoS parameters has been obtained. Using the obtained EPPPs and applying the pair-wise additive approximation, one could calculate accurately the thermodynamics functions such as total energy. The results of such calculations for the total energy of the liquid methane obtained via the EPPPs from different EoSs indicate a good agreement with the experimental data. Physical interpretation for the state dependencies of the obtained EPPPs from given EoSs is also presented.

Many physical and chemical properties depend strongly on the molecular interaction potential. Attempts have been made to relate the molecular interaction potential to experimentally measurable properties, like the second virial coefficient¹ and transport properties². Since the relation between the thermodynamic properties and the intermolecular interactions is very complicated, it has been impossible to introduce a unique function for the interaction potential which gives a satisfactory agreement with the experimental data of both the equilibrium and transport properties, except for the noble gases for which accurate pair potential expressions are known.

The investigation of the molecular interactions in dense systems is more complicated than those of the isolated pair mainly due to the non-additive contribution of the potential. However, it is known that the major contribution is due to the additive pair potential. The interaction potential of an isolated pair is quite different from that in the presence of the other molecules³⁻⁶. This difference can be attributed to the effect of the medium on the molecular charge distribution and the long-range interactions. Based on such an idea, the concept of an average 'effective pair potential' (EPP) was introduced³, in order to write the configurational potential energy as the sum of only

the nearest neighbor potential energies with the EPP interactions. Such a pair potential is considered as an isolated pair potential in which the medium effect and all long-range interactions of a given pair with remaining molecules are both added. The mathematical form of the EPP is considered to be the same as that of the isolated pair potential. But, the parameters of the former are state dependent.

During the present investigation, the internal energy of the liquid methane has been obtained based on the pair-wise additive approximation using the (12,6) Lennard-Jones function as the EPP. This internal energy is then related to the internal pressure via equation of state (EoS) expression. The relation between the potential parameters with EoS parameters is then used for calculating the pair potential parameters. By such a method, the effective pair potential parameters (EPPP) through some given EoSs for dense fluids are calculated. A physical interpretation for the state dependencies of the obtained EPPPs from given EoSs is also presented.

Theoretical

The aim is to relate the EPPP with the EoS parameters via internal pressure (p_{int}). The thermodynamic function $p_{\text{int}} = (\partial U / \partial V)_T$ shows that p_{int} has a relationship with the internal energy (U). We will

use the EoSs that work well in the dense region. On the other hand, the LJ (12,6) pair potential has been chosen for the EPP since it is simple enough and works well especially for simple molecules such as methane as our sample for calculations. Indeed, using the LJ(12, 6) potential for the EPP along with the pair wise additive approximation for the intermolecular interaction in dense fluids, and considering only the nearest neighbor interactions, makes it possible to accurately obtain the configurational energy of the system. This procedure was carried out for the MSRK EoS as:

$$p = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad \dots (1)$$

Here,

$$a = a_c \alpha, \quad a_c = 0.4286R^2T_c^2/p_c, \quad b = 0.08664RT_c/p_c$$

$$\alpha = [1 + C_1(1 - \sqrt{T_r})]^2,$$

$$\alpha' = (\partial\alpha/\partial T)_V = -C_1[1 + C_1(1 - \sqrt{T_r})]/T_c\sqrt{T_r} \text{ for } T_r > 1$$

For methane, we have:

$$p_c = 4.59 \text{ MPa}, \quad T_c = 190.564 \text{ K}, \quad C_1 = 0.5472$$

The thermodynamic relation between internal pressure (p_{int}) and total pressure (p) is:

$$p_{\text{int}} = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad \dots (2)$$

So, one can obtain p_{int} of an EoS by deriving the thermal pressure, $p_{\text{ther}} = T(\partial p/\partial T)_V$, from total pressure and then subtracting the result from total pressure to get:

$$\left(\frac{\partial U}{\partial V}\right)_T = -(p - p_{\text{ther}}) = \frac{a - a'T}{V(V+b)} \quad \dots (3)$$

where $a' = (\partial a/\partial T)_V$.

From the Eq. (3), one may derive the internal energy (U) of the fluid as:

$$U = (a'T - a) \left(\frac{1}{V} - \frac{b}{2V^2} + \frac{b^2}{3V^3} - \frac{b^3}{4V^4} + \Lambda \right) + C(T) \quad \dots (4a)$$

where $C(T)$ is a temperature-dependent constant, and indeed is equal to the thermal energy of the molecules and incorporated to the other temperature dependent terms in the result). The configurational energy based on the EPP is given as:

$$U = \frac{N}{2}(A\rho)\varepsilon \left[\left(\frac{\sigma}{\bar{r}}\right)^9 - \left(\frac{\sigma}{\bar{r}}\right)^3 \right] = \frac{N}{2}A\varepsilon \left[\frac{\sigma^9}{\bar{r}^{12}} - \frac{\sigma^3}{\bar{r}^6} \right] \\ = \frac{N}{2}A\varepsilon \left[\frac{\sigma^9}{V^4} - \frac{\sigma^3}{V^2} \right] \quad \dots (4)$$

where \bar{r} is the average intermolecular distance that is proportional to $V^{1/3}$, the term of $(A\rho)$ is the coordination number (the quantity that is proportional to the number density, (ρ) , A is a constant, the well depth (ε) and the distance (σ) are the effective pair potential parameters. By comparing the internal energy (U) via Eq. (3) with Eq. (4), we get the relation between the EPPP with MSRK EoS parameters as:

$$\sigma^3 = b, \quad \varepsilon = (a - a'T)/A, \quad A = 4.42666e - 3 \quad \dots (5)$$

The term 'A' was calculated by applying the experimental data to Eq. (5) and choosing one point for which we have the EPPPs. This has been done by using the data from our earlier studies³. The same procedures have been used for the following EoSs. Thus, MBWR EoS may be given⁸ as:

$$p = \frac{RT}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^5} + \frac{E}{V^3} e^{-F/V^2} + \frac{EF}{V^5} e^{-F/V^2} \quad \dots (6)$$

$$B = B^c T_r \left[1 + b_1(1 - T_r^{-1.6}) + b_2(1 - T_r^{-3.2}) \right] \\ C = C^c T_r \left[1 + c_1(1/T_r - 1) + c_2(1/T_r - 1)^2 + c_3(1/T_r - 1)^3 \right] \\ E = E^c T_r \left[1 + e_1(1/T_r - 1) + e_2(1/T_r - 1)^2 + e_3(1/T_r - 1)^3 \right]$$

The parameters of this EoS are: $B^c = -1827447$; $C^c = -13151719$; $D^c = 913223083$; $E^c = 82824210$; $F = 7074$; $b_1 = -1.2921$; $b_2 = 0.002971$; $c_1 = 3.8695$; $c_2 = -0.4995$; $c_3 = -0.1977$; $e_1 = 2.6529$; $e_2 = 1.9280$; $e_3 = -0.1697$

This EoS gives the internal energy as:

$$U = \frac{B - B'T}{V} + \frac{(C + E) - (C' + E')T}{2V^2} + \frac{D}{4V^4} + \Lambda \quad \dots (7)$$

with the definitions,

$$\begin{aligned}
 B' &= (\partial B/\partial T)_V = B^c T_c^{-1} \left[1 + b_1(1 - T_r^{-1.6}) \right. \\
 &\quad \left. + b_2(1 - T_r^{-3.2}) + 1.6b_1 T_r^{-1.6} + 3.2b_2 T_r^{-3.2} \right] \\
 C' &= C^c T_c^{-1} \left[1 + c_1(1/T_r - 1) + c_2(1/T_r - 1)^2 + c_3(1/T_r - 1)^3 \right. \\
 &\quad \left. - c_1 T_r^{-1} - 2c_2 T_r^{-1}(1/T_r - 1) - 3c_3 T_r^{-1}(1/T_r - 1)^2 \right] \\
 E' &= E^c T_c^{-1} \left[1 + e_1(1/T_r - 1) + e_2(1/T_r - 1)^2 + e_3(1/T_r - 1)^3 \right. \\
 &\quad \left. - e_1 T_r^{-1} - 2e_2 T_r^{-1}(1/T_r - 1) - 3e_3 T_r^{-1}(1/T_r - 1)^2 \right]
 \end{aligned} \dots (8)$$

and the EPPPs as:

$$\sigma^3 = \left[\frac{D}{4(B'T - B)} \right]^{1/3}, \quad \varepsilon = \frac{D}{4A\sigma^9}, \quad A = 5580.0549 \dots (9)$$

'A' has been calculated the same as that explained for the previous EoS.

Thus, KT EoS may be given⁸ as:

$$B = B^c \left[(1 - b_1 - b_2 - b_3) T_r + b_1 + b_2/T_r + b_3/T_r^2 \right] \dots (10)$$

$$\begin{aligned}
 p &= \frac{RT}{V - b} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^6} + \frac{E}{V^7} + F e^{GV} \\
 &\quad + \frac{e}{1 + f(V - g)^2}
 \end{aligned}$$

$$C = C^c \left[(1 - c_1 - c_2 - c_3 - c_4) T_r^2 + c_1 T_r + c_2 + c_3/T_r + c_4/T_r^2 \right]$$

$$D = D^c \left[(1 - d_1 - d_2 - d_3) T_r + d_1 + d_2/T_r + d_3/T_r^2 \right]$$

The parameters of this EoS are: $b=13.073$; $B^c=-2724985$; $C^c = 70211844$; $D^c = -2.612e13$; $E=7.912e14$; $F=154453$; $G = -0.12284$; $e = -8.03642$; $f=3.3564e-4$; $g = 86.513$; $F = 1.3713$; $b_2 = -0.4610$; $b_3=0.2565$; $c_1 = -1.8080$; $c_2 = 4.2445$; $c_3 = -2.7420$; $c_4=1.0949$; $d_1=1.4533$; $d_2= -0.2786$; $d_3 = 0.0945$.

The KT EoS gives the internal energy as:

$$U = \frac{B - B'T}{V} + \frac{(C - C'T)}{2V^2} + \frac{(D - D'T)}{5V^5} + \frac{E}{6V^6} + \Lambda \dots (11)$$

$$\begin{aligned}
 B' &= (\partial B/\partial T)_V = B^c T_c^{-1} \left[(1 - b_1 - b_2 - b_3) \right. \\
 &\quad \left. - b_2/T_r^2 - 2b_3/T_r^3 \right]
 \end{aligned}$$

$$C' = C^c T_c^{-1} \left[2(1 - c_1 - c_2 - c_3 - c_4) T_r + c_1 - c_3/T_r^2 - 2c_4/T_r^3 \right]$$

$$D' = D^c T_c^{-1} \left[(1 - d_1 - d_2 - d_3) - d_2/T_r^2 - 2d_3/T_r^3 \right]$$

$$\sigma^3 = \left[\frac{0.4(D - D'T)}{(C'T - C)} \right]^{1/3}, \quad \varepsilon = \frac{(C'T - C)}{2A\sigma^3},$$

$$A = -2055.4111 \dots (12)$$

MPR1 EoS may be given⁹ as:

$$p = \frac{RT}{V - b} - \frac{a}{V^2 + 2Vb - b^2} \dots (13)$$

$$a = a_c \alpha, \quad a_c = 0.45724R^2 T_c^2 / p_c,$$

$$b = 0.0778RT_c / p_c$$

$$\alpha = \left[1 + m'(1 - \sqrt{T_r}) \right]^2, \quad m' = 1.21m$$

$$m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3,$$

for methane: $\omega = 0.004$

$$\begin{aligned}
 U &= (a'T - a) \left(\frac{1}{V} - \frac{2.4142b}{V^2} + \frac{5.8283b^2}{V^3} \right. \\
 &\quad \left. - \frac{14.0707b^3}{V^4} + \Lambda \right) \dots (14)
 \end{aligned}$$

$$\alpha' = (\partial \alpha/\partial T)_V = -m' \left[1 + m'(1 - \sqrt{T_r}) \right] / T_c \sqrt{T_r},$$

$$a' = a_c \alpha', \quad \sigma^3 = 2.4142b,$$

$$\varepsilon = (a - a'T)/A, \quad A = 5.88851e - 3 \dots (15)$$

Thus, LIR EoS may be given¹⁰ as:

$$p = \frac{RT}{V} + \frac{ART}{V^3} + \frac{BRT}{V^5} \dots (16)$$

$$A = A' - A'/RT, \quad B = -B'/RT$$

Here, A' and B' are the slopes of the lines of A and B in terms of $1/T$, and A and B are the intercept and slope of the line $(Z - 1)V^2$ against ρ^2 respectively. Z is the compressibility factor and V is the molar volume and ρ is the density number of the fluid. Thus,

$$U = -\frac{A'}{2V^2} - \frac{B'}{4V^4} \dots (17)$$

$$\sigma^3 = (B'/2A')^{1/2}, \quad \varepsilon = 2A'^2/B' \dots (18)$$

NB EoS may be given¹¹ as:

$$p = \frac{RT}{V-b} - \frac{a}{(V+b/\sqrt{3})^2} \quad \dots (19)$$

$$a = a_c \alpha, \quad a_c = 0.45724R^2T_c^2/p_c, \\ b = 0.0778RT_c/p_c$$

$$\alpha = \frac{b_1}{T_r} + \frac{b_2}{T_r^2} + \frac{b_3}{T_r^3} \quad \text{for } T_r > 1$$

$$b_1 = 0.25(12 - 11m + m^2), \quad b_2 = 0.5(-6 + 9m - m^2), \\ b_3 = 0.25(4 - 7m + m^2) \\ m = 0.4857 + 1.6308\omega - 0.2089\omega^2, \\ \text{for methane: } \omega = 0.004$$

$$\alpha' = (\partial\alpha/\partial T)_V = -T_c^{-1} \left(\frac{b_1}{T_r^2} + \frac{2b_2}{T_r^3} + \frac{3b_3}{T_r^4} \right)$$

$$U = (a'T - a) \left(\frac{1}{V} - \frac{b/\sqrt{3}}{V^2} + \frac{(b/\sqrt{3})^2}{V^3} - \frac{(b/\sqrt{3})^3}{V^4} + \Lambda \right) \quad \dots (20)$$

$$\sigma^3 = b/\sqrt{3}, \quad \varepsilon = (a - a'T)/A, \\ A = 5.46735e - 3 \quad \dots (21)$$

HK EoS may be given¹² as:

$$p = \frac{RT}{V-b} - \frac{a}{V^2 + Vbc - b^2(c-1)} \quad \dots (22)$$

$$a = a_c \alpha, \quad a_c = \Omega_a R^2 T_c^2 / p_c, \quad b = \Omega_b RT_c / p_c$$

$$\alpha = 1 - (0.6258 + 1.5227\omega) \ln T_r \\ + (0.1533 + 0.41\omega) (\ln T_r)^2$$

$$\Omega_a = 1 - 3\eta + 3\eta^2 + \beta\eta(3 - 6\eta + \beta\eta), \quad \Omega_b = \beta\eta, \\ c = 1 + (1 - 3\eta) / \beta\eta$$

$$\beta = 0.10770 + 0.76405\eta - 1.24282\eta^2 + 0.9610\eta^3$$

$$\eta = 0.3211 - 0.08\omega + 0.0384\omega^2, \\ \text{for methane: } \omega = 0.004$$

$$U = (a'T - a) \left(\frac{1}{V} - \frac{bc}{2V^2} + \frac{b^2(c-1)}{3V^3} + \Lambda \right) \quad \dots (23)$$

$$\alpha' = (\partial\alpha/\partial T)_V = [-(0.6258 + 1.5227\omega) \\ + 2(0.1533 + 0.41\omega) \ln T_r] / T_r T_c^2$$

$$\sigma^3 = b(c^2/4 + 1.5c - 1), \quad \varepsilon = (a - a'T)/A, \\ A = 3.506477e - 3 \quad \dots (24)$$

vdW11 EoS can be given¹³ as:

$$p = \frac{RT}{V+t-b} - \frac{a}{(V+t)^2} \quad \dots (25)$$

$$a = a_c \alpha, \quad a_c = 0.421875R^2T_c^2/p_c, \quad b = 0.125RT_c/p_c$$

$$\alpha = [1 + m(1 - \sqrt{T_r})]^2$$

$$m = 0.48553 + 1.624\omega - 0.21884\omega^2, \\ \text{for methane: } \omega = 0.004$$

$$z_c = 0.289 - 0.701\omega - 0.0207\omega^2,$$

$$\beta = -7.35356 - 24.5176\omega + 9.19829\omega^2$$

$$t_c = (0.375 - z_c)RT_c/p_c,$$

$$t_0 = (0.03479 + 0.0937\omega - 0.16606\omega^2 \\ + 0.12499\omega^3)RT_c/p_c$$

$$t = t_0 + (t_c - t_0)e^{\beta|1-T_r|}$$

$$U = \left(\frac{I}{V} + \frac{II}{V^2} + \frac{III}{V^3} + \frac{IV}{V^4} + \Lambda \right) \quad \dots (26)$$

$$I = (a'T - a) + RT^2 t',$$

$$II = (a - a'T)t - RT^2 t'(t-b) - at'T$$

$$III = (a'T - a)t^2 + RT^2 t'(t-b)^2 + 2at'tT,$$

$$IV = (a - a'T)t^3 - RT^2 t'(t-b)^3 - 3at't^2T$$

$$t' = (-\beta/T_c)(t_c - t_0)e^{\beta|1-T_r|},$$

$$\alpha' = (\partial\alpha/\partial T)_V = -m [1 + m(1 - \sqrt{T_r})] / T_c \sqrt{T_r}$$

$$\sigma^3 = -II/I, \quad \varepsilon = -I/A, \quad A = 4.901237e - 3 \\ \dots (27)$$

Table 1 — Calculated depth potential well parameter (ϵ/k) values at given temperatures for various EoSs

| T (K) | MSRK | MBWR | KT | MPR1 | LIR | NB | HK | vdW11 | MMM |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 250 | | 573.57 | 573.57 | 573.57 | 573.57 | 573.57 | 573.55 | | |
| 280 | 541.20 | 536.13 | 556.84 | 554.40 | 538.87 | 548.48 | 532.53 | 594.05 | |
| 300 | 520.99 | 514.53 | 548.74 | 542.19 | | 531.98 | 508.89 | 592.56 | |
| 330 | 492.46 | 486.08 | 536.23 | 524.61 | | 507.98 | 477.87 | 580.67 | |
| 350 | 474.51 | 469.30 | 526.07 | 513.33 | 474.51 | 492.62 | 459.68 | 569.88 | 484.76 |
| 380 | 449.01 | 446.80 | 506.66 | 497.01 | 449.01 | 470.67 | 435.48 | 552.22 | 465.23 |
| 400 | 432.87 | 433.31 | 490.54 | 486.48 | 432.87 | 456.80 | 421.11 | 540.19 | 453.45 |
| 460 | 388.06 | 398.57 | 426.15 | 456.38 | 388.06 | 418.78 | 384.77 | 504.84 | 422.84 |
| 480 | 374.19 | 388.55 | 399.57 | 446.78 | 374.19 | 407.25 | 374.52 | 493.46 | 413.94 |
| 500 | 360.80 | 379.17 | 370.66 | 437.39 | 360.80 | 396.25 | 365.05 | 482.30 | 405.58 |
| 520 | 347.86 | 370.38 | 339.63 | 428.18 | 347.86 | 385.77 | 356.28 | 471.36 | 397.70 |
| 540 | 335.34 | 362.10 | 306.71 | 419.15 | 335.34 | 375.77 | 348.14 | 460.62 | 390.26 |
| 580 | 311.49 | 346.94 | | 401.57 | 311.49 | 357.10 | 333.57 | 439.71 | 376.57 |
| 600 | 300.12 | 339.97 | | 393.01 | 300.12 | 348.40 | 327.03 | 429.53 | 370.24 |

Table 2 — The calculated distance potential parameter value (σA) at given temperatures for various EoSs

| T (K) | MBWR | KT | LIR | vdW11 |
|-------|------|------|------|-------|
| 120 | | | 3.28 | |
| 140 | | | 3.27 | |
| 160 | | | 3.31 | |
| 180 | | | | |
| 200 | | | 3.32 | |
| 220 | | | 3.34 | |
| 250 | 1.90 | 4.31 | 3.36 | 2.31 |
| 280 | 1.92 | 4.32 | 3.38 | 2.64 |
| 300 | 1.93 | 4.33 | | 2.69 |
| 330 | 1.94 | 4.34 | | 2.72 |
| 350 | 1.95 | 4.35 | 3.42 | 2.72 |
| 380 | 1.96 | 4.36 | 3.44 | 2.72 |
| 400 | 1.96 | 4.38 | 3.45 | 2.72 |
| 460 | 1.98 | 4.43 | 3.49 | 2.72 |
| 480 | 1.99 | 4.46 | 3.51 | 2.72 |
| 500 | 1.99 | 4.49 | 3.52 | 2.72 |
| 520 | 2.00 | 4.52 | 3.53 | 2.72 |
| 540 | 2.00 | 4.56 | 3.54 | 2.72 |
| 580 | 2.01 | 4.67 | 3.57 | 2.72 |
| 600 | 2.02 | 4.73 | 3.58 | 2.72 |

Thus, MMM EoS may be given¹⁴ as:

$$p = \frac{(V + 1.3191b)RT}{V(V - b)} - \frac{a}{T^{1/2}v(V + b)} \quad \dots (28)$$

$$a = 0.48748R^2T_c^{2.5}/p_c, \quad b = 0.064462RT_c/p_c$$

$$U = \frac{0.5a}{T^{1/2}} \left(-\frac{1}{V} + \frac{b}{2V^2} - \frac{b^2}{3V^3} + \frac{b^3}{4V^4} + \Lambda \right) \quad \dots (29)$$

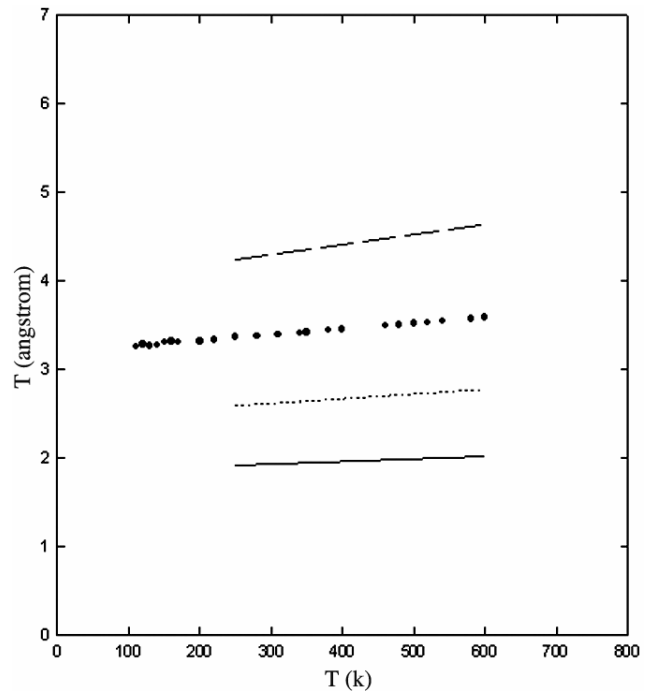


Fig. 1 — Behaviour of distance potential parameter (σA) in terms of temperature (T) for various EoSs: MBWR (—), KT (---), LIR(●), vdW11(...).

$$\sigma^3 = 0.75b, \quad \epsilon = 0.2962963a/AT^{1/2}, \quad A = 1.188007e - 3 \quad \dots (30)$$

Results and Discussion

Table 1 shows the results of calculation for the ϵ parameter through the equations presented for the selected EoSs. The results of such a calculation for

the σ parameter are presented in Table 2. The results of Tables 1 and 2 indicate that for all EoSs, the \mathcal{E} parameter decreases with increasing temperature, while the σ parameter increases with increasing temperature. This is in accordance with the results of our previous calculations for EPPP via LIR³ and VIM⁵ EoSs.

The \mathcal{E} and σ values obtained from different EoSs show differences in their amounts, in special in the case of σ (Fig. 1). However, this difference is such that if one EoS predicts the greater value for \mathcal{E} than LIR, it gives the smaller value for the σ than LIR at the same temperature, and these differences compensate each other. So, the difference in the obtained \mathcal{E} and σ values from different EoSs shows the sensitivity of the method to the used EoS, so that the more precious EoS will give more precious \mathcal{E} and σ values. This reality may be considered as superior of the LIR EoS to the other EoSs, since the LIR EoS in the prediction of the behaviour of many types of liquids in the dense region has been very successful¹⁰.

In order to evaluate the calculated EPPPs, we recalculated the total energy of the fluid, E , via the relation:

$$E = 3RT + \frac{AN_A \mathcal{E}}{2} \left[\frac{\sigma^{12}}{V^4} - \frac{\sigma^6}{V^3} \right] \quad \dots (31)$$

where the term of $3RT$ is equal to the translational plus rotational degrees of freedom contributions for methane molecule in the total energy and N_A is the Avogadro's number. Such calculations have been done for the EPPPs obtained from different EoSs and the results of these calculations have been compared with the experimental data. The mean deviations in the predictions of the E are listed in Table 3, which show that agreement between the calculated and experimental data is good.

Conclusions

In the dense fluids because of the effects of the medium molecules on the charge distribution of a given pair molecule, the intermolecular potential is different from an isolated pair. To evaluate the medium effects, it was assumed that the form of the potential function is the same as isolated one though the parameters of former are state dependent. The dependency for dense fluids is only with temperature¹⁵. We have calculated here the EPPPs via

Table 3 — Relative deviation in the calculated total energy (E) calculated via Eq. (31) and using the EPP parameters given in Tables 1 and 2 for the selected EoSs with the experimental data

| EoS | $10^2 \times (E - E_c) / E_c$ |
|-------|-------------------------------|
| MSRK | 11.90 |
| MBWR | 12.34 |
| KT | 11.82 |
| MPR1 | 9.10 |
| LIR | <1 |
| NB | 9.74 |
| HK | 9.81 |
| vdW11 | 8.74 |
| MMM | 9.18 |

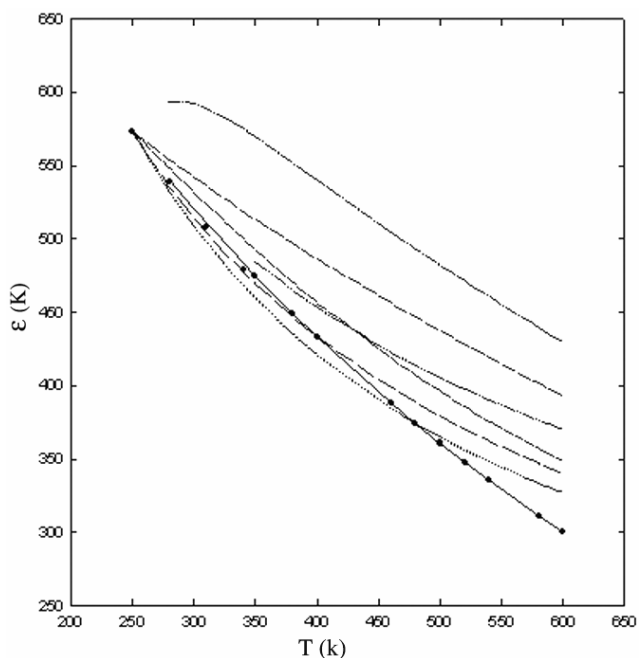


Fig. 2 — Depth potential (\mathcal{E}/k) in terms of temperature (T) for various EoSs: MSRK (—), MBWR(---), MPR1(....), LIR(●), NB(○), HK(×), vdW11(□), MMM(△).

EoS expressions at different temperatures. The results show that the method is accurate and the results for different EoSs are in good agreement with each other, at least in their trends. Figures 1 and 2 show that for all selected EoSs, the predicted parameter σ (in the MBWR, KT, LIR, and vdW11 EoSs) increases with increasing temperature and the predicted parameter \mathcal{E} decreases with increasing temperature. This behaviour is logical. It is because, when temperature increases, the kinetic energy of molecules increases and then the intermolecular pair potential between a pair of molecules becomes weaker. This leads to a smaller

magnitude for the parameter ε and then to the larger magnitude for the parameter σ .

Using the obtained EPPPs and applying the pairwise additive approximation, it will be possible to calculate the total energy and then the other thermodynamic functions via thermodynamic relations accurately. This calculation has been carried out for the total energy of liquid methane by using the EPPPs obtained from different EoSs. The relative deviations in the calculated total energies, via the obtained EPPPs from different EoSs, with experimental data for all selected EoSs are about 10% (Table 3).

Nomenclature

| | |
|---------------|--|
| p | Pressure, N m^{-2} |
| R | Gas constant, $\text{J mol}^{-1} \text{K}^{-1}$ |
| T | Temperature, K |
| V | Molar volume, $\text{m}^3 \text{mol}^{-1}$ |
| T_c | Critical temperature, K |
| p_c | Critical pressure, N m^{-2} |
| V_c | Critical volume, $\text{m}^3 \text{mol}^{-1}$ |
| T_r | Reduced temperature |
| U | Configurational energy, J mol^{-1} |
| ε | Well depth, K |
| σ | Molecular diameter, nm |
| r | Intermolecular distance, nm |
| k | Boltzmann constant, $\text{J molecule}^{-1} \text{K}^{-1}$ |
| N_A | Avogadro's number |

| | |
|----------|-------------------------------------|
| ρ | Density number, mol m^{-3} |
| Z | Compressibility factor |
| ω | Acentric factor |
| E | Total energy, J mol^{-1} |

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