

# COMPARING DIFFERENT METHODS FOR PREDICTION OF LIQUEFIED NATURAL GAS DENSITIES

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## ABSTRACT

The densities of several liquefied natural gas (LNG) mixtures and pure methane using different equations of state and correlations have been predicted and compared with the experimental values. The equations of state were Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), Usdin-McAuliffe (UM), Volume Translated SRK (VT SRK), Nasrifar-Moshfeghian (NM) and modified Nasrifar-Moshfeghian (MNM). The correlations were Rackett-Spencer-Danner (RSD), Hankinson-Thompson (HT), Nasrifar-Moshfeghian (NML), and simplified Nasrifar-Moshfeghian (S-NML). It has been attempted to choose the most popular EoSs and correlations with the highest accuracy for predicting the density of LNG mixtures.

For the systems under study, the NM EoS had the least average absolute deviation of liquid density among the equations of state evaluated, and the NML correlation predicted the LNG liquid density more accurately than the other liquid density correlations. The accuracy of this method for prediction of methane liquid density is also as good as that of RSD's and HT's. Moreover, using the NM EoS, density as a function of temperature and pressure for the whole phase envelope has been plotted. Results, especially near the critical point, show good compatibility between the bubble and dew point densities. The predicted values of methane vapor and liquid density/specific volume up to near the critical point based on these equations of state are also given. No fitting or adjustable parameters were used for any of the EoSs or correlations.

**Keywords:** Liquid density, LNG, Equation of state, Phase envelope, Methane

## I. INTRODUCTION

Liquid density is needed for process simulation and equipment design. For example, accurate predictions of liquid density are needed for calculation of pressure drop in a piping and vessel sizing. Accurate liquid density is also essential for custody transfer.

Liquid density ranges from a few hundred above thousand to couple of 100 kg/m<sup>3</sup>. Liquid densities are sometime expressed in terms of specific gravity or API gravity. The specific gravity,  $\gamma$ , is defined as

$$\gamma = \frac{\text{Liquid density at standard condition}}{\text{Liquid water density at standard condition}}$$

and the API (American Petroleum Index) gravity is

$$API = \frac{141.5}{\gamma} - 131.5$$

Depending on the applications, three different methods can be used to compute liquid density in addition to direct laboratory measurement. These methods are (a) charts and monographs, (b) correlations and (c) EoS, of which the correlations are usually the most accurate.

For the LNG density measurement and calculation, one of the standard procedures practiced in industry is ISO 6578. This procedure specifies the calculations to be made to adjust the volume of a liquid from the conditions at measurement to the equivalent volume of liquid or vapor at a standard temperature and pressure, or to the equivalent mass or energy (calorific content). Annexes A to H of this procedure form an integral part of this standard.

The cubic equations of state give accurate results for prediction of vapor-liquid equilibria, especially for non-polar or slightly polar systems. Furthermore, these equations could be used to predict vapor densities, enthalpy and entropy of vaporization accurately. These characteristics make them popular, although their accuracy for liquid density prediction is not as good as correlations. The popular equations of state such as PR (Peng and Robinson, 1976) and SRK (Soave, 1972) predict liquid density with average absolute error about 8%, much more than the correlations (Nasrifar and Moshfeghian, 1999).

Equations of state, as powerful tools, are used in many commercial simulation softwares for prediction of phase behavior and thermodynamic properties. Moreover, they need only a few parameters (usually two or three) which normally are obtained from critical properties. These advantages encourage the researchers to augment EoS ability more than before, especially, liquid density.

The UM EOS (Usdin and McAuliffe, 1976) developed a new cubic EoS with relatively good results for liquid density. This EoS, in addition to the critical temperature, pressure and acentric factor, needs two other parameters: experimental critical compressibility factor,  $Z_c$ , and a fifth parameter, so-called critical compressibility parameter,  $Z_c^*$ .

Nasrifar and Moshfeghian (2001) developed a cubic equation of state (NM EoS) that predicts liquid densities of light hydrocarbons accurately. This EoS, such as PR and SRK, needs two parameters that are obtained from the critical properties and acentric factor for pure components. Results show that this equation predicts phase equilibria of light hydrocarbons as good as PR or SRK equations of state (Nasrifar and Moshfeghian, 2002a, 2002b). More recently, they modify this equation for heavy hydrocarbons which is named MNM EoS (Nasrifar and Moshfeghian, 2004).

In this work the densities of several LNG mixtures and methane have been predicted using six equations of state and four liquid density correlations. Moreover, the calculated results are compared with the experimental data. Among the existing correlations, HT method (Hankinson and Thomson, 1979), RSD method (Spencer and Danner, 1972) NML (Nasrifar and Moshfeghian, 1998) and the simplified NML or S-NML methods (Nasrifar and Moshfeghian, 2004) have been evaluated.

## II. EQUATIONS OF STATE AND CORRELATIONS

In this section, the equations of state and the correlations used in this study are presented:

### 1. SRK and PR Equations of State

These two equations (Soave, 1972 and Peng and Robinson, 1976) predict phase equilibria, vapor volume and other properties of pure compounds accurately. But the liquid density is predicted inaccurately with an average absolute error about 8%. These two EoSs are well known and their details are presented in Table A1 and A2 in the Appendix.

### 2. Volume Translated SRK

The SRK liquid volume is corrected in this method. The details of this method are given by Peneloux et al. (1982) and its expression is given in Table A1 of Appendix.

### 3. UM Equation of State

The Usdin and McAuliffe (1976) EoS, needs five parameters for predicting the properties of pure compounds. The dimensionless form of this equation is

$$Z^3 + (D - B - 1)Z^2 + (A - D - BD)Z - AB = 0 \quad (1)$$

where:

$$A = \left[ \sum_{i=1}^N x_i \left( Ac_i \alpha_i(T) \frac{Pr_i}{Tr_i} \right)^{0.5} \right]^2 \quad (2)$$

$$B = \sum_{i=1}^N x_i Bc_i \frac{Pr_i}{Tr_i} \quad (3)$$

$$D = \sum_{i=1}^N x_i Dc_i \frac{Pr_i}{Tr_i} \quad (4)$$

The parameter  $\alpha(T)$  for each compound is defined as follows:

$$\alpha(T) = \left[ 1.0 + m(1.0 - Tr^{0.5}) \right]^2 \quad (5)$$

and

$$m = \begin{cases} 0.48049 + 4.516\omega Z_c^* + [0.67713(\omega - 0.35) - 0.02](Tr - 0.7) & Tr \leq 0.7 \\ 0.48049 + 4.516\omega Z_c^* + [37.78\omega Z_c^{*2} + 0.78662](Tr - 0.7)^2 & 0.7 < Tr \leq 1.0 \end{cases} \quad (6)$$

$Z_c^*$  is the critical compressibility parameter which differs from the experimental compressibility factor and for each component has been given by Usdin and McAuliffe (1976).  $Dc$  is the most positive real root of the following equation:

$$Dc^3 + (6Zc - 1)Dc^2 + 3Zc(4Zc - 1)Dc + Zc^3(8Zc - 3) = 0 \quad (7)$$

then  $Ac$  and  $Bc$  could be obtained from the following equations for each compound:

$$Bc = Dc + 3Zc - 1 \quad (8)$$

$$Ac = Zc^3 / Bc \quad (9)$$

As mentioned above, five parameters are required for each compound:  $Tc$ ,  $Pc$ ,  $\omega$ ,  $Z_c$ , and  $Z_c^*$ .

### 4. NM Equation of State

This cubic equation has been developed recently by Nasrifar and Moshfeghian (2001). In dimensionless form, this EoS is written as:

$$Z^3 - (1 - B)Z^2 + (A - 2B - 4B^2)Z - (AB - 2B^2 - 2B^3) = 0 \quad (10)$$

where  $A$  is defined as follows:

$$A = \frac{Pa_{mix}}{(RT)^2} \quad (11)$$

$$a_{mix} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (12)$$

$$a_i = ac_i \left[ 1 + m_{a_i} (1 - \theta_i^{0.5}) \right]^2 \quad (13)$$

$$ac_i = 0.497926 \frac{(RTc_i)^2}{Pc_i} \quad (14)$$

$$m_{a_i} = \sqrt{\frac{a_{pt_i}}{ac_i}} - 1 \quad (15)$$

$$a_{pt_i} = 29.7056 b_{pt_i} RT_{pt_i} \quad (16)$$

Other parameters are expressed as follows:

$$B = \frac{Pb_{mix}}{RT} \quad (17)$$

$$b_{mix} = \sum_{i=1}^N x_i bc_i \left[ 1 + m_{b_i} (1 - \theta_i) \right] \quad (18)$$

$$bc_i = \left( 0.094451 \frac{RTc_i}{Pc_i} \right) \quad (19)$$

$$m_{b_i} = \frac{b_{pt_i}}{bc_i} - 1 \quad (20)$$

$$b_{pt_i} = bc_i \left( 1 - 0.1519\omega_i - 3.9462\omega_i^2 + 7.0538\omega_i^3 \right) \quad (21)$$

$$\theta_i = \begin{cases} \frac{T - T_{pt_i}}{Tc_i - T_{pt_i}} & T > T_{pt_i} \\ 0 & T < T_{pt_i} \end{cases} \quad (22)$$

$$T_{pt_i} = Tc_i \left( 0.2498 + 0.3359\omega_i - 0.1037\omega_i^2 \right) \quad (23)$$

### 5. MNM Equation of State

This cubic equation is the modified form of NM EoS for heavy hydrocarbons, Nasrifar and Moshfeghian (2004). In the dimensionless form, this EoS is the same as NM EOS:

$$Z^3 - (1 - B)Z^2 + (A - 2B - 4B^2)Z - (AB - 2B^2 - 2B^3) = 0 \quad (24)$$

where:

$$T_i^* = (0.1771 + 0.017\omega_i + 0.5691\omega_i^2 - 0.3379\omega_i^3)T_{c_i} \quad (25)$$

$$T_{t_i} = (0.2552 + 0.2407\omega_i - 0.051\omega_i^2)T_{c_i} \quad (26)$$

$$b_{c_i} = 0.094451 \frac{RT_{c_i}}{P_{c_i}} \quad (27)$$

$$b_{t_i} = (1.045 - 1.1262\omega_i + 1.2799\omega_i^2 - 0.7456\omega_i^3)b_{c_i} \quad (28)$$

$$mm_i = \frac{b_{t_i}}{b_{c_i}} - 1 \quad (29)$$

$$\theta_i = \frac{T - T_{t_i}}{T_{c_i} - T_{t_i}} \quad (30)$$

$$b_i = b_{c_i} [1 + mm_i(1 - \theta_i)] \quad (31)$$

$$\alpha_i = 29.7056 - 24.4338 \frac{\left[ \exp\left(\frac{T_i^*}{T}\right) - \exp\left(\frac{T_i^*}{T_{t_i}}\right) \right]}{\left[ \exp\left(\frac{T_i^*}{T_{c_i}}\right) - \exp\left(\frac{T_i^*}{T_{t_i}}\right) \right]} \quad (32)$$

$$a_i = \alpha_i b_i RT \quad (33)$$

For mixtures the following mixing rules can be used.

$$b_{mix} = \sum_{i=1}^N x_i b_i \quad (34)$$

$$B = \frac{b_{mix} P}{RT} \quad (35)$$

$$a_{mix} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i a_j} \quad (36)$$

$$A = \frac{Pa_{mix}}{(RT)^2} \quad (37)$$

## 6. HT (COSTALD) Correlation

The COSTALD correlation (Hankinson and Thomson, 1979) is given by:

$$\frac{V_s}{V^*} = V_R^{(0)}(1 - \omega_{SRK} V_R^\delta) \quad (38)$$

where:

$$V_R^{(0)} = 1 - 1.52816(1 - Tr)^{1/3} + 1.43907(1 - Tr)^{2/3} - 0.81446(1 - Tr) + 0.190454(1 - Tr)^{4/3} \quad \text{for } 0.25 < Tr < 0.95 \quad (39)$$

$$V_R^\delta = \frac{-0.296123 + 0.386914Tr - 0.0427258Tr^2 - 0.0480645Tr^3}{Tr - 1.00001} \quad \text{for } 0.25 < Tr < 1.0 \quad (40)$$

where  $\omega_{SRK}$  is the optimized value of the acentric factor based on the SRK EOS. The parameter  $V^*$  is the pure component characteristic volume which was given by Hankinson and Thomson (1979).

For mixtures, the following mixing rules are used:

$$\omega_{SRK_{mix}} = \sum_{i=1}^N x_i \omega_{SRK_i} \quad (41)$$

$$V_{mix}^* = \frac{1}{4} \left[ \sum_{i=1}^N x_i V_i^* + 3 \left( \sum_{i=1}^N x_i (V_i^*)^{1/3} \right) \left( \sum_{i=1}^N x_i (V_i^*)^{2/3} \right) \right] \quad (42)$$

$$Tc_{mix} = \frac{1}{V_{mix}^*} \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{Tc_i V_i^* Tc_j V_j^*} \quad (43)$$

## 7. RSD Correlation

Spencer and Danner (1972) modified the liquid density correlation of Rackett (1970). Using the improved correlation, the saturated liquid density is calculated from:

$$1/\rho_s = V_s = \frac{RT_c}{P_c} Z_{RA} \left[ 1 + (1 - Tr)^{2.17} \right] \quad (44)$$

The parameter  $Z_{RA}$  is the improved compressibility factor which is given by Spencer and Danner (1972). In this work the values of  $Z_{RA}$  reported by Mchaweh et al. (2004) have been used. This parameter is given in Table A4 of Appendix.

For mixtures the following mixing rules, given by Spencer and Danner (1973), are used:

$$Z_{RA} = \sum_{i=1}^N x_i Z_{RAi} \quad (45)$$

$$Tc = \frac{1}{Vc} \sum_{i=1}^N x_i Tc_i Vc_i \quad (46)$$

$$Vc = \sum_{i=1}^N x_i Vc_i \quad (47)$$

$$Tc/Pc = \sum_{i=1}^N x_i (Tc_i/Pc_i) \quad (48)$$

### 8. NML Correlation

Nasrifar and Moshfeghian (1998) presented the following correlation for predicting saturated liquid densities:

$$\rho_r = \frac{\rho_s}{\rho_c} = \rho_0 \left[ 1 + \delta_{NML} (f(Tr) - 1)^{1/3} \right] \quad (49)$$

$$f(Tr) = \left[ 1 + c_1 (1 - Tr^{0.5}) + c_2 (1 - Tr^{0.5})^2 + c_3 (1 - Tr^{0.5})^3 \right]^2 \quad \text{for } Tr < 1.0 \quad (50-a)$$

$$f(Tr) = \left[ 1 + c_1 (1 - Tr^{0.5}) \right]^2 \quad \text{for } Tr > 1.0 \quad (50-b)$$

$$\rho_0 = 1 + 1.1688(1 - Tr/f(Tr))^{1/3} + 1.8177(1 - Tr/f(Tr))^{2/3} - 2.6581(1 - Tr/f(Tr)) + 2.1613(1 - Tr/f(Tr))^{4/3} \quad (51)$$

where the parameters  $c_1$  through  $c_3$  and  $\delta_{NML}$  were reported in their paper. In this work, the values of  $\delta_{NML}$  reported by Mchaweh et al. (2004) are used. This parameter is given in Table A4 of Appendix. It is worth noting that the parameters  $c_1$  to  $c_3$  were optimized using vapor pressure data. They are not liquid density fitting parameters. Also note that Eq.(50) is the temperature dependent parameter of the PSRK EOS Holderbaum and Gmehling (1991). In fact Eqs.(49-50) are used with the PSRK EoS to augment the liquid density prediction capability of the PSRK EoS.

For mixtures, the following relations could be used:

$$\delta_{NMLmix} = \sum_{i=1}^N x_i \delta_{NMLi} \quad (52)$$

$$Tc_{mix} = \sum_{i=1}^N x_i Tc_i \quad (53)$$

$$\rho_{cmix}^{-3/4} = \sum_{i=1}^N x_i \rho_{ci}^{-3/4} \quad (54)$$

$$f(Tr)_{mix} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{f(Tr)_i f(Tr)_j} \quad (55)$$

### 9. Simple NML Correlation

This method uses the same temperature dependency term as SRK EoS, Mchaweh et al.(2004). In this method, the temperature dependent term of NML method for component i, Eq. (50), is replaced by the following equation:

$$f(Tr)_i = \left[ 1 + m_i \left( 1 - \sqrt{Tr_i} \right) \right]^2 \quad (56)$$

where  $m_i$  is defined as for the SRK EoS:

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \quad (57)$$

For mixtures, the same mixing rules as the NML method are used. It should be noted that the optimized values of  $\delta_{S-NML}$  reported by Mchaweh et al. (2004) should be used. This parameter for the compounds used in this work is given in Table A4 of Appendix.

## III. RESULTS AND DISCUSSIONS

The compositions of the LNG systems used in this study have been given in Table 1. The required parameters and critical properties needed for equations of states and correlations are presented in Tables A3 and A4 of Appendix. The predicted liquid densities for these systems based on the above equations of state, have been given in Table 2. Table 3 shows the same results based on the liquid density correlations.

As shown in Table 2, the predicted liquid densities based on the PR EoS show the maximum average error, where this value for the NM EoS is the lowest. Table 3 indicates that among the correlations, the NML has the least error.

The differences between the liquid density errors for different equations of state as shown in Table 2 are considerable: rating from about 10% for PR EoS to about 0.5% for the NM EoS. The accuracies of the correlations, as indicated in Table 3, have the same order of magnitude.

Furthermore, the NM EoS and the correlations in Table 3 have the comparable accuracy for prediction of the liquid density.

Figure 1 shows saturated liquid and vapor densities as a function of pressure for mixture A. The relations between densities of liquid and vapor as a function of saturated temperature are also shown in Figure 2. Figures 1 and 2 are typical and the same density envelopes were obtained for mixtures B through E.

In these figures, the liquid and vapor densities have been calculated by the NM EoS. The experimental liquid density data are also shown in these figures. As can be seen, the calculated results are in good agreement with the experimental data.

These two figures indicate that the compatibilities between the dew point and bubble point curves are excellent. Equations of state usually exhibit anomaly near the critical point and the calculated curves may not approach each other. While, as indicated in these figures, for NM EoS not only the continuity of the predicted dew and bubble curves but also their slope are the same at these points.

**Table 1: The Compositions of the LNG Systems used in this Work (Haynes, 1982)**

| Comp. | Mixture |       |       |       |       |
|-------|---------|-------|-------|-------|-------|
|       | A       | B     | C     | D     | E     |
| C1    | 85.34   | 75.44 | 75.70 | 74.27 | 90.07 |
| C2    | 7.90    | 15.40 | 13.59 | 16.51 | 6.54  |
| C3    | 4.73    | 6.95  | 6.74  | 6.55  | 2.20  |
| i-C4  | 0.85    | 0.98  | 1.34  | 0.84  | 0.29  |
| n-C4  | 0.99    | 1.06  | 1.33  | 0.89  | 0.28  |
| i-C5  | 0.10    | 0.09  | 0.22  | 0.07  | 0.01  |
| n-C5  | 0.09    | 0.08  | 0.22  | 0.07  | 0.01  |
| N2    | 0.00    | 0.00  | 0.86  | 0.80  | 0.60  |

**Table 2: Predicted Liquid Density using Different Equations of State**

| Point             | Gas Mix. | T (K) | P (MPa) | $\rho_{exp}$ (kg/m <sup>3</sup> ) | Dev% <sup>**</sup> |                |                |               |                |                |
|-------------------|----------|-------|---------|-----------------------------------|--------------------|----------------|----------------|---------------|----------------|----------------|
|                   |          |       |         |                                   | PR                 | SRK            | UM             | VTSRK         | NM             | MNM            |
| 1                 | A        | 110   | 0.0787  | 484.09                            | 10.8866            | -1.5290        | -1.3798        | 1.6387        | -0.6789        | -2.0262        |
| 2                 | A        | 115   | 0.1172  | 477.32                            | 10.9356            | -1.5510        | -2.6406        | 1.5696        | -0.2892        | -1.5474        |
| 3                 | A        | 120   | 0.1686  | 470.57                            | 10.9132            | -1.6356        | -3.9959        | 1.4341        | 0.0964         | -1.1109        |
| 4                 | A        | 125   | 0.2351  | 463.69                            | 10.8480            | -1.7569        | -5.4207        | 1.2591        | 0.4731         | -0.6919        |
| 5                 | A        | 130   | 0.3210  | 456.64                            | 10.7434            | -1.9107        | -6.9026        | 1.0485        | 0.8124         | -0.2864        |
| 6                 | B        | 110   | 0.0723  | 511.88                            | 10.1017            | -2.1361        | 0.6561         | 1.5784        | -1.2479        | -2.2451        |
| 7                 | B        | 115   | 0.1081  | 505.74                            | 10.1350            | -2.1678        | -0.4541        | 1.4981        | -0.9509        | -1.8589        |
| 8                 | B        | 120   | 0.1549  | 499.23                            | 10.1975            | -2.1734        | -1.5476        | 1.4432        | -0.5657        | -1.4297        |
| 9                 | B        | 125   | 0.2153  | 492.51                            | 10.2521            | -2.1854        | -2.6535        | 1.3798        | -0.1610        | -0.9897        |
| 10                | C        | 110   | 0.1155  | 515.28                            | 9.9821             | -2.2432        | 0.3950         | 1.5070        | -1.1671        | -2.1525        |
| 11                | C        | 115   | 0.1595  | 508.72                            | 10.0936            | -2.2049        | -0.6373        | 1.4986        | -0.7879        | -1.6961        |
| 12                | C        | 120   | 0.2155  | 502.28                            | 10.1287            | -2.2344        | -1.7446        | 1.4183        | -0.4159        | -1.2908        |
| 13                | C        | 125   | 0.2873  | 495.75                            | 10.1286            | -2.2942        | -2.8784        | 1.3047        | -0.0487        | -0.9000        |
| 14                | C        | 130   | 0.3744  | 489.08                            | 10.0999            | -2.3783        | -4.0127        | 1.1643        | 0.2807         | -0.5171        |
| 15                | D        | 110   | 0.1158  | 512.97                            | 10.2169            | -2.0390        | 0.7605         | 1.6437        | -1.2176        | -2.2023        |
| 16                | D        | 115   | 0.1584  | 506.68                            | 10.2693            | -2.0538        | -0.3077        | 1.5809        | -0.9015        | -1.7962        |
| 17                | D        | 120   | 0.2093  | 499.88                            | 10.3813            | -2.0157        | -1.3389        | 1.5713        | -0.4716        | -1.3196        |
| 18                | D        | 125   | 0.2853  | 493.27                            | 10.3986            | -2.0605        | -2.4212        | 1.4740        | -0.1018        | -0.9107        |
| 19                | E        | 115   | 0.1456  | 454.01                            | 11.6354            | -1.0197        | -3.9518        | 1.5670        | -0.0262        | -1.5352        |
| 20                | E        | 120   | 0.2024  | 446.95                            | 11.5240            | -1.1862        | -5.5226        | 1.3506        | 0.3372         | -1.1009        |
| 21                | E        | 125   | 0.2762  | 439.42                            | 11.4340            | -1.3314        | -7.1464        | 1.1542        | 0.7491         | -0.6231        |
| 22                | E        | 130   | 0.3698  | 431.97                            | 11.2174            | -1.5853        | -8.9384        | 0.8443        | 1.0622         | -0.2321        |
| AAPD <sup>*</sup> |          |       |         |                                   | <b>10.5692</b>     | <b>1.8951</b>  | <b>2.9867</b>  | <b>1.4058</b> | <b>0.5837</b>  | <b>1.2938</b>  |
| APD <sup>**</sup> |          |       |         |                                   | <b>10.5692</b>     | <b>-1.8951</b> | <b>-2.8220</b> | <b>1.4058</b> | <b>-0.2373</b> | <b>-1.2938</b> |

\* Experimental data by Haynes(1982)

\*\*Dev%=100 × (ρ<sub>cal</sub>-ρ<sub>exp</sub>)/(ρ<sub>exp</sub>)

+AAPD=(100/no. of points)∑<sub>i=1</sub><sup>no. of points</sup> |ρ<sub>cal<sub>i</sub></sub> - ρ<sub>exp<sub>i</sub></sub> | / ρ<sub>exp<sub>i</sub></sub>

++APD=(100/no. of points)∑<sub>i=1</sub><sup>no. of points</sup> (ρ<sub>cal<sub>i</sub></sub> - ρ<sub>exp<sub>i</sub></sub>) / ρ<sub>exp<sub>i</sub></sub>

Table 3: Predicted Liquid Density using Different Correlations

| Point             | Gas Mix. | T (K) | P (MPa) | $\rho_{exp}^*$ (kg/m <sup>3</sup> ) | Dev%**        |               |                |                |
|-------------------|----------|-------|---------|-------------------------------------|---------------|---------------|----------------|----------------|
|                   |          |       |         |                                     | RSD           | HT            | NML            | S-NML          |
| 1                 | A        | 110   | 0.0787  | 484.09                              | 0.5586        | 0.3604        | -0.0197        | -0.1552        |
| 2                 | A        | 115   | 0.1172  | 477.32                              | 0.7088        | 0.3481        | -0.0984        | -0.2370        |
| 3                 | A        | 120   | 0.1686  | 470.57                              | 0.8348        | 0.3031        | -0.2159        | -0.3633        |
| 4                 | A        | 125   | 0.2351  | 463.69                              | 0.9663        | 0.2534        | -0.3439        | -0.5056        |
| 5                 | A        | 130   | 0.3210  | 456.64                              | 1.1105        | 0.2040        | -0.4775        | -0.6583        |
| 6                 | B        | 110   | 0.0723  | 511.88                              | 0.3397        | 0.4235        | 0.0288         | -0.1800        |
| 7                 | B        | 115   | 0.1081  | 505.74                              | 0.4204        | 0.3451        | -0.1067        | -0.3089        |
| 8                 | B        | 120   | 0.1549  | 499.23                              | 0.5590        | 0.3177        | -0.1992        | -0.3993        |
| 9                 | B        | 125   | 0.2153  | 492.51                              | 0.7241        | 0.3088        | -0.2811        | -0.4833        |
| 10                | C        | 110   | 0.1155  | 515.28                              | 0.3718        | 0.4501        | -0.0150        | -0.2422        |
| 11                | C        | 115   | 0.1595  | 508.72                              | 0.5365        | 0.4409        | -0.0863        | -0.3080        |
| 12                | C        | 120   | 0.2155  | 502.28                              | 0.6632        | 0.3859        | -0.2115        | -0.4318        |
| 13                | C        | 125   | 0.2873  | 495.75                              | 0.7919        | 0.3238        | -0.3521        | -0.5750        |
| 14                | C        | 130   | 0.3744  | 489.08                              | 0.9316        | 0.2622        | -0.5006        | -0.7295        |
| 15                | D        | 110   | 0.1158  | 512.97                              | 0.3859        | 0.4306        | 0.0501         | -0.1481        |
| 16                | D        | 115   | 0.1584  | 506.68                              | 0.4819        | 0.3707        | -0.0681        | -0.2594        |
| 17                | D        | 120   | 0.2093  | 499.88                              | 0.6639        | 0.3899        | -0.1156        | -0.3043        |
| 18                | D        | 125   | 0.2853  | 493.27                              | 0.7916        | 0.3469        | -0.2328        | -0.4230        |
| 19                | E        | 115   | 0.1456  | 454.01                              | 0.5115        | 0.1649        | -0.1307        | -0.1681        |
| 20                | E        | 120   | 0.2024  | 446.95                              | 0.5797        | 0.1151        | -0.2473        | -0.3011        |
| 21                | E        | 125   | 0.2762  | 439.42                              | 0.7205        | 0.1299        | -0.3023        | -0.3792        |
| 22                | E        | 130   | 0.3698  | 431.97                              | 0.8062        | 0.0799        | -0.4240        | -0.5299        |
| AAPD <sup>+</sup> |          |       |         |                                     | <b>0.6572</b> | <b>0.3070</b> | <b>0.2049</b>  | <b>0.3678</b>  |
| APD <sup>++</sup> |          |       |         |                                     | <b>0.6572</b> | <b>0.3070</b> | <b>-0.1977</b> | <b>-0.3678</b> |

\* Experimental data by Haynes (1982)

\*\* Dev% =  $100 \times (\rho_{cal} - \rho_{exp}) / \rho_{exp}$

+ AAPD =  $(100 / \text{no. of points}) \sum_{i=1}^{\text{no. of points}} |\rho_{cal_i} - \rho_{exp_i}| / \rho_{exp_i}$

++ APD =  $(100 / \text{no. of points}) \sum_{i=1}^{\text{no. of points}} (\rho_{cal_i} - \rho_{exp_i}) / \rho_{exp_i}$

The predicted values of methane liquid density have been given In Table 4. Comparing these results with that obtained for the LNG systems indicates that except for the UM EOS, the same trend has been observed. The UM EoS can not predict the liquid compressibility factor near the critical point, however, for lower temperatures, the same accuracies as those of the LNG systems have been obtained. The accuracy of the NM EoS, even near the critical point, is the best.

Table 5 shows the predicted vapor volume for the EoSs. In this case, the accuracies of EoSs are good enough with the maximum average absolute percent error of 3.8%. The SRK predictions, especially near the critical conditions, to some extent are better than the others.

Figures 3 and 4 show saturated liquid and vapor densities of methane as a function of pressure and temperature, respectively. As in Figures 1 and 2, the calculated values are based on NM EoS.

Table 6 indicates that the HT method, followed very closely by NML, has the least liquid density error; however, near the critical point its error is somehow greater than the RSD and NML methods. In summery, for the liquid density of pure methane all of the considered correlations have almost the same accuracy.

The results of the S-NML method indicates that if NML correlation is used in conjunction with the SRK EoS, replacing Eq.(50) with Eq. (56), for the temperature dependency of parameter  $a$ , will improve the accuracy of SRK EoS for predicting liquid density.

The NML and S-NML methods have only one liquid density adjustable parameter ( $\delta$ ). This parameter has a small value near zero. Nasrifar and Moshfeghian have reported that in cases where  $\delta$  value is not available, a zero value may be used at the cost of losing accuracy slightly. In this case, the NML method is fully predictive with an average absolute deviation better than 2% (Nasrifar and Moshfeghian, 1998). Finally, in case where  $c_1$  to  $c_3$  have not been determined for a specific compound, one can avoid them by using the ordinary SRK EoS temperature dependent term instead of Eq.(50).

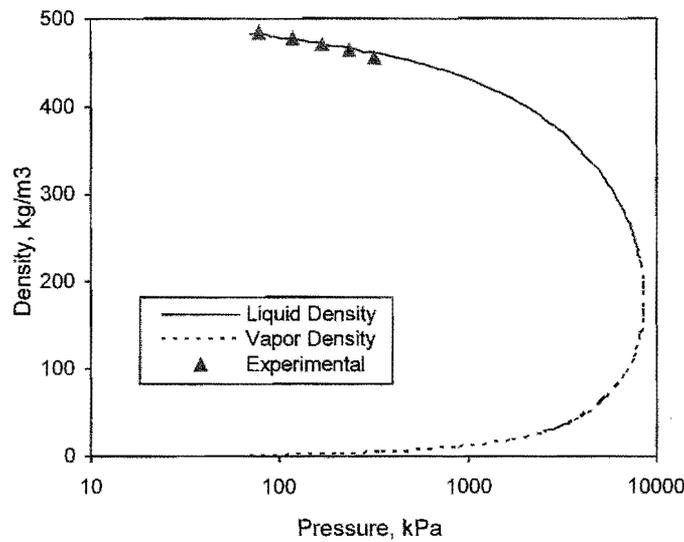


Figure 1: Saturated Liquid and Vapor Densities as a Function of Pressure for Gas Mixture A by NM EoS

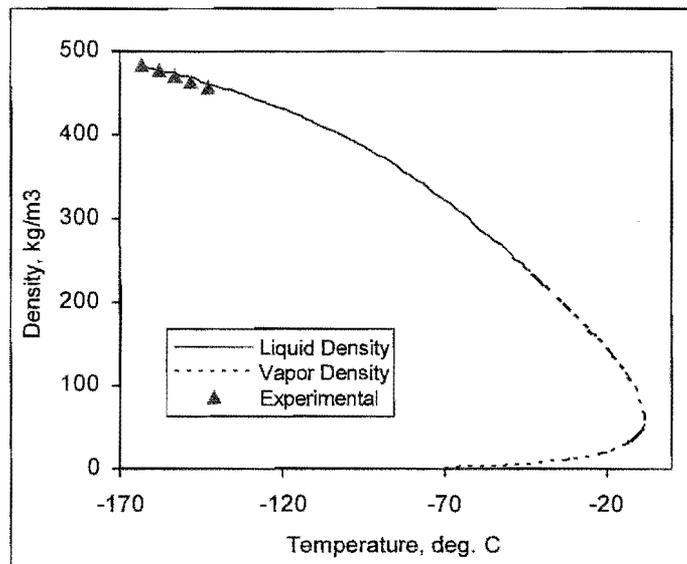


Figure 2: Saturated Liquid and Vapor Densities as a Function of Temperature for Gas Mixture A by the NM EoS

**Table 4: Predicted Liquid Density of Methane using Different Equations of State**

| Point             | T (K) | P (kPa) | $\rho_{exp}^*$ (kg/m <sup>3</sup> ) | Dev% <sup>**</sup> |                |                 |                |                |                |
|-------------------|-------|---------|-------------------------------------|--------------------|----------------|-----------------|----------------|----------------|----------------|
|                   |       |         |                                     | PR                 | SRK            | UM              | VTSRK          | NM             | MNM            |
| 1                 | 100.0 | 33.78   | 440.67                              | 12.2956            | -0.3322        | -1.5603         | 1.7051         | -1.0813        | -3.2605        |
| 2                 | 102.8 | 44.75   | 436.98                              | 12.2214            | -0.4402        | -2.4406         | 1.5752         | -0.8809        | -3.0167        |
| 3                 | 105.6 | 58.19   | 433.14                              | 12.1581            | -0.5383        | -3.3383         | 1.4551         | -0.6629        | -2.7560        |
| 4                 | 108.3 | 74.60   | 429.30                              | 12.0629            | -0.6643        | -4.2943         | 1.3060         | -0.4650        | -2.4185        |
| 5                 | 111.1 | 95.15   | 425.29                              | 11.9757            | -0.7827        | -5.2760         | 1.1643         | -0.2517        | -2.2591        |
| 6                 | 113.9 | 119.97  | 421.61                              | 11.7675            | -1.0075        | -6.3989         | 0.9134         | -0.1378        | -2.1004        |
| 7                 | 116.7 | 149.69  | 417.12                              | 11.7334            | -1.0772        | -7.4223         | 0.8201         | 0.1406         | -1.7782        |
| 8                 | 119.4 | 183.40  | 412.80                              | 11.6161            | -1.2197        | -8.5792         | 0.6522         | 0.3541         | -1.5218        |
| 9                 | 122.2 | 223.39  | 408.63                              | 11.4117            | -1.4380        | -9.8757         | 0.4064         | 0.4985         | -1.3330        |
| 10                | 125.0 | 268.90  | 404.47                              | 11.1588            | -1.6976        | -11.3054        | 0.1179         | 0.6088         | -1.1774        |
| 11                | 127.8 | 319.92  | 400.46                              | 10.8088            | -2.0414        | -12.9401        | -0.2568        | 0.6408         | -1.0987        |
| 12                | 130.6 | 377.83  | 395.50                              | 10.6696            | -2.1967        | -14.5822        | -0.4403        | 0.8746         | -0.8215        |
| 13                | 133.3 | 444.71  | 391.65                              | 10.1571            | -2.6795        | -16.7522        | -0.9578        | 0.7780         | -0.8689        |
| 14                | 136.1 | 518.49  | 386.85                              | 9.8476             | -2.9801        | -18.6370        | -1.2904        | 0.8776         | -0.7233        |
| 15                | 138.9 | 603.98  | 382.36                              | 9.3777             | -3.4190        | -21.0396        | -1.7644        | 0.8398         | -0.7127        |
| 16                | 141.7 | 696.37  | 376.92                              | 9.1042             | -3.6809        | -24.6134        | -2.0592        | 0.9952         | -0.5117        |
| 17                | 144.4 | 797.72  | 371.63                              | 8.7003             | -4.0537        | -               | -2.4676        | 1.0424         | -0.4172        |
| 18                | 147.2 | 910.11  | 366.50                              | 8.1560             | -4.5456        | -               | -2.9978        | 0.9709         | -0.4394        |
| 19                | 150.0 | 1034.21 | 361.54                              | 7.4594             | -5.1662        | -               | -3.6596        | 0.7684         | -0.5908        |
| 20                | 152.8 | 1170.04 | 355.93                              | 6.8361             | -5.7156        | -               | -4.2501        | 0.6462         | -0.6628        |
| 21                | 155.6 | 1320.35 | 349.68                              | 6.2794             | -6.1986        | -               | -4.7740        | 0.5988         | -0.6607        |
| 22                | 158.3 | 1481.68 | 343.76                              | 5.4765             | -6.8904        | -               | -5.5110        | 0.3322         | -0.8749        |
| 23                | 161.1 | 1654.74 | 337.19                              | 4.6986             | -7.5503        | -               | -6.2169        | 0.1034         | -1.0516        |
| 24                | 163.9 | 1842.97 | 330.94                              | 3.6272             | -8.4578        | -               | -7.1752        | -0.3938        | -1.4934        |
| 25                | 166.7 | 2047.74 | 324.21                              | 2.4798             | -9.4185        | -               | -8.1887        | -0.9530        | -1.9962        |
| 26                | 169.4 | 2268.38 | 316.53                              | 1.3662             | -10.3330       | -               | -9.1571        | -1.4668        | -2.4537        |
| 27                | 172.2 | 2509.69 | 308.04                              | 0.2006             | -11.2727       | -               | -10.1527       | -2.0210        | -2.9500        |
| 28                | 175.0 | 2764.80 | 299.39                              | -1.3322            | -12.5139       | -               | -11.4562       | -2.9167        | -3.7843        |
| 29                | 177.8 | 3033.69 | 290.26                              | -3.2720            | -14.0875       | -               | -13.0991       | -4.1923        | -4.9953        |
| 30                | 180.6 | 3323.27 | 279.04                              | -5.2590            | -15.6639       | -               | -14.7488       | -5.4953        | -6.2333        |
| 31                | 183.3 | 3633.54 | 267.03                              | -8.1187            | -17.9662       | -               | -17.1384       | -7.6329        | -8.3016        |
| 32                | 186.1 | 3964.49 | 251.81                              | -12.0646           | -21.1849       | -               | -20.4650       | -10.7443       | -11.3564       |
| AAPD'             |       |         |                                     | <b>8.2404</b>      | <b>5.8504</b>  | <b>10.5660</b>  | <b>4.9482</b>  | <b>1.5739</b>  | <b>2.3319</b>  |
| APD <sup>++</sup> |       |         |                                     | <b>6.3625</b>      | <b>-5.8504</b> | <b>-10.5660</b> | <b>-4.3160</b> | <b>-0.8820</b> | <b>-2.3319</b> |

\* Experimental data by (ASHRAE, 1989)

\*\* Dev% =  $100 \times (\rho_{cal} - \rho_{exp}) / (\rho_{exp})$

+ AAPD =  $(100/\text{no. of points}) \sum_{i=1}^{\text{no. of points}} |\rho_{cal_i} - \rho_{exp_i}| / \rho_{exp_i}$

++ APD =  $(100/\text{no. of points}) \sum_{i=1}^{\text{no. of points}} (\rho_{cal_i} - \rho_{exp_i}) / \rho_{exp_i}$

‡ The UM EOS can not predict the liquid compressibility factor

Table 5: Predicted Vapor Volume of Methane using Different Equations of State

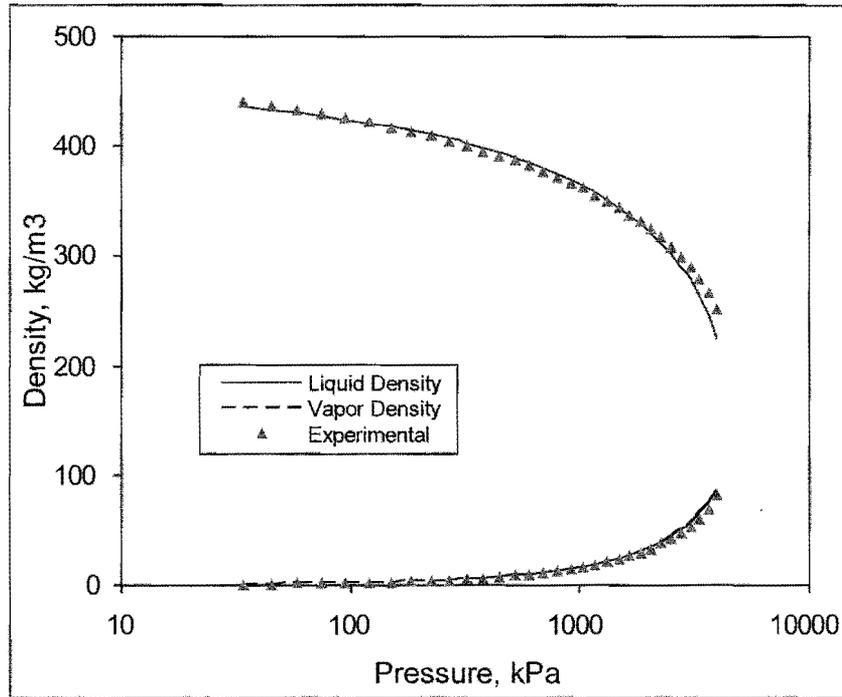
| Point | T (K) | P (kPa) | v <sub>exp</sub> *, (m <sup>3</sup> /kg) | Dev%**        |               |               |               |                |                |
|-------|-------|---------|--|---------------|---------------|---------------|---------------|----------------|----------------|
|       |       |         |  | PR            | SRK           | UM            | VTSRK         | NM             | MNM            |
| 1     | 100.0 | 33.78   | 1.5008                                   | 0.7749        | 0.8105        | 1.4387        | 0.8105        | 0.7544         | 0.7223         |
| 2     | 102.8 | 44.75   | 1.1662                                   | 0.2864        | 0.3342        | 1.0889        | 0.3342        | 0.2595         | 0.2226         |
| 3     | 105.6 | 58.19   | 0.9121                                   | 0.8585        | 0.9219        | 1.8230        | 0.9219        | 0.8233         | 0.7812         |
| 4     | 108.3 | 74.60   | 0.7267                                   | 0.8811        | 0.9634        | 2.0197        | 0.9634        | 0.8360         | 0.7887         |
| 5     | 111.1 | 95.15   | 0.5812                                   | 0.8728        | 0.9788        | 2.2130        | 0.9788        | 0.8152         | 0.7624         |
| 6     | 113.9 | 119.97  | 0.4670                                   | 1.4260        | 1.5614        | 2.9974        | 1.5614        | 1.3528         | 1.2939         |
| 7     | 116.7 | 149.69  | 0.3814                                   | 1.2188        | 1.3885        | 3.0323        | 1.3885        | 1.1275         | 1.0628         |
| 8     | 119.4 | 183.40  | 0.3165                                   | 1.1551        | 1.3639        | 3.2151        | 1.3639        | 1.0428         | 0.9731         |
| 9     | 122.2 | 223.39  | 0.2635                                   | 1.2136        | 1.4691        | 3.5483        | 1.4691        | 1.0763         | 1.0011         |
| 10    | 125.0 | 268.90  | 0.2223                                   | 0.9877        | 1.2956        | 3.5985        | 1.2956        | 0.8222         | 0.7424         |
| 11    | 127.8 | 319.92  | 0.1892                                   | 0.9318        | 1.2989        | 3.8249        | 1.2989        | 0.7343         | 0.6503         |
| 12    | 130.6 | 377.83  | 0.1617                                   | 1.0448        | 1.4799        | 4.2371        | 1.4799        | 0.8103         | 0.7225         |
| 13    | 133.3 | 444.71  | 0.1392                                   | 0.5881        | 1.0992        | 4.0870        | 1.0992        | 0.3122         | 0.2211         |
| 14    | 136.1 | 518.49  | 0.1199                                   | 0.9753        | 1.5750        | 4.7965        | 1.5750        | 0.6512         | 0.5568         |
| 15    | 138.9 | 603.98  | 0.1036                                   | 0.7968        | 1.4964        | 4.9550        | 1.4964        | 0.4183         | 0.3211         |
| 16    | 141.7 | 696.37  | 0.0905                                   | 0.5284        | 1.3354        | 4.9988        | 1.3354        | 0.0914         | -0.0073        |
| 17    | 144.4 | 797.72  | 0.0793                                   | 0.4975        | 1.4249        | 5.2839        | 1.4249        | -0.0051        | -0.1045        |
| 18    | 147.2 | 910.11  | 0.0699                                   | 0.0031        | 1.0603        | 5.0876        | 1.0603        | -0.5698        | -0.6689        |
| 19    | 150.0 | 1034.21 | 0.0614                                   | 0.0884        | 1.2968        | 5.5034        | 1.2968        | -0.5659        | -0.6644        |
| 20    | 152.8 | 1170.04 | 0.0541                                   | 0.1397        | 1.5154        | 5.8798        | 1.5154        | -0.6042        | -0.7009        |
| 21    | 155.6 | 1320.35 | 0.0479                                   | -0.3479       | 1.2081        | 5.6975        | 1.2081        | -1.1872        | -1.2807        |
| 22    | 158.3 | 1481.68 | 0.0426                                   | -0.6970       | 1.0567        | 5.6316        | 1.0567        | -1.6398        | -1.7287        |
| 23    | 161.1 | 1654.74 | 0.0379                                   | -0.9795       | 0.9904        | 5.6025        | 0.9904        | -2.0340        | -2.1167        |
| 24    | 163.9 | 1842.97 | 0.0338                                   | -1.4140       | 0.7930        | 5.3974        | 0.7930        | -2.5884        | -2.6631        |
| 25    | 166.7 | 2047.74 | 0.0300                                   | -1.7114       | 0.7636        | 5.3253        | 0.7636        | -3.0183        | -3.0834        |
| 26    | 169.4 | 2268.38 | 0.0267                                   | -2.1329       | 0.6362        | 5.0849        | 0.6362        | -3.5807        | -3.6339        |
| 27    | 172.2 | 2509.69 | 0.0237                                   | -2.7485       | 0.3505        | 4.6341        | 0.3505        | -4.3477        | -4.3864        |
| 28    | 175.0 | 2764.80 | 0.0211                                   | -3.4963       | -0.0409       | 3.9381        | -0.0409       | -5.2508        | -5.2718        |
| 29    | 177.8 | 3033.69 | 0.0188                                   | -4.3937       | -0.5543       | 2.9264        | -0.5543       | -6.3037        | -6.3040        |
| 30    | 180.6 | 3323.27 | 0.0167                                   | -5.5391       | -1.2711       | 1.5082        | -1.2711       | -7.6049        | -7.5810        |
| 31    | 183.3 | 3633.54 | 0.0145                                   | -5.5698       | -0.7503       | 1.0151        | -0.7503       | -7.8149        | -7.7627        |
| 32    | 186.1 | 3964.49 | 0.0124                                   | -5.6285       | -0.1614       | -0.1371       | -0.1614       | -8.0306        | -7.9497        |
| AAPD* |       |         |  | <b>1.5602</b> | <b>1.0389</b> | <b>3.7665</b> | <b>1.0389</b> | <b>2.0961</b>  | <b>2.0853</b>  |
| APD** |       |         |  | <b>0.6059</b> | <b>0.8653</b> | <b>3.7579</b> | <b>0.8653</b> | <b>-1.3506</b> | <b>-1.4089</b> |

\* Experimental data by (ASHRAE, 1989)

\*\* Dev% = 100 × (v<sub>cal</sub> - v<sub>exp</sub>) / (v<sub>exp</sub>)

+ AAPD = (100/no. of points) ∑<sub>i=1</sub><sup>no. of points</sup> |v<sub>cal<sub>i</sub></sub> - v<sub>exp<sub>i</sub></sub>| / v<sub>exp<sub>i</sub></sub>

++ APD = (100/no. of points) ∑<sub>i=1</sub><sup>no. of points</sup> (v<sub>cal<sub>i</sub></sub> - v<sub>exp<sub>i</sub></sub>) / v<sub>exp<sub>i</sub></sub>



: Saturated Liquid and Vapor Densities as a Function of Pressure for Methane by the NM EoS

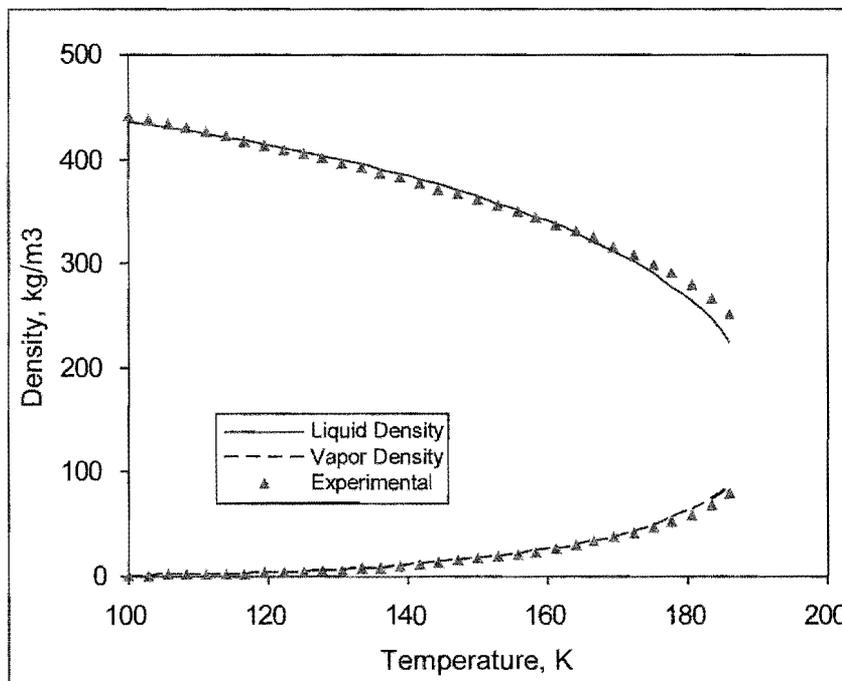


Figure 4: Saturated Liquid and Vapor Densities as a Function of Temperature for Methane by the NM EoS

**Table 6: Predicted Liquid Density of Methane using Different Correlations**

| Point                   | T<br>(K) | P<br>(MPa) | $\rho_{exp}^*$<br>(kg/m <sup>3</sup> ) | Dev% <sup>**</sup> |                |                |                |
|-------------------------|----------|------------|--|--------------------|----------------|----------------|----------------|
|                         |          |            |  | RSD                | HT             | NML            | S-NML          |
| 1                       | 100.0    | 33.78      | 440.67                                 | -0.3618            | -0.1387        | -0.1056        | 0.0062         |
| 2                       | 102.8    | 44.75      | 436.98                                 | -0.4109            | -0.1960        | -0.1917        | -0.0797        |
| 3                       | 105.6    | 58.19      | 433.14                                 | -0.4364            | -0.2286        | -0.2530        | -0.1441        |
| 4                       | 108.3    | 74.60      | 429.30                                 | -0.4753            | -0.2737        | -0.3268        | -0.2239        |
| 5                       | 111.1    | 95.15      | 425.29                                 | -0.4915            | -0.2949        | -0.3763        | -0.2826        |
| 6                       | 113.9    | 119.97     | 421.61                                 | -0.5983            | -0.4063        | -0.5152        | -0.4337        |
| 7                       | 116.7    | 149.69     | 417.12                                 | -0.5323            | -0.3436        | -0.4793        | -0.4129        |
| 8                       | 119.4    | 183.40     | 412.80                                 | -0.5206            | -0.3344        | -0.4958        | -0.4474        |
| 9                       | 122.2    | 223.39     | 408.63                                 | -0.5659            | -0.3819        | -0.5673        | -0.5397        |
| 10                      | 125.0    | 268.90     | 404.47                                 | -0.6320            | -0.4495        | -0.6573        | -0.6531        |
| 11                      | 127.8    | 319.92     | 400.46                                 | -0.7604            | -0.5792        | -0.8072        | -0.8290        |
| 12                      | 130.6    | 377.83     | 395.50                                 | -0.6738            | -0.4931        | -0.7395        | -0.7897        |
| 13                      | 133.3    | 444.71     | 391.65                                 | -0.8948            | -0.7152        | -0.9765        | -1.0571        |
| 14                      | 136.1    | 518.49     | 386.85                                 | -0.9021            | -0.7232        | -0.9970        | -1.1101        |
| 15                      | 138.9    | 603.98     | 382.36                                 | -1.0227            | -0.8452        | -1.1277        | -1.2751        |
| 16                      | 141.7    | 696.37     | 376.92                                 | -0.9275            | -0.7515        | -1.0396        | -1.2232        |
| 17                      | 144.4    | 797.72     | 371.63                                 | -0.9092            | -0.7360        | -1.0251        | -1.2461        |
| 18                      | 147.2    | 910.11     | 366.50                                 | -0.9750            | -0.8060        | -1.0912        | -1.3505        |
| 19                      | 150.0    | 1034.21    | 361.54                                 | -1.1327            | -0.9700        | -1.2457        | -1.5439        |
| 20                      | 152.8    | 1170.04    | 355.93                                 | -1.1693            | -1.0154        | -1.2759        | -1.6139        |
| 21                      | 155.6    | 1320.35    | 349.68                                 | -1.0859            | -0.9438        | -1.1829        | -1.5612        |
| 22                      | 158.3    | 1481.68    | 343.76                                 | -1.1604            | -1.0347        | -1.2446        | -1.6627        |
| 23                      | 161.1    | 1654.74    | 337.19                                 | -1.1302            | -1.0260        | -1.1990        | -1.6566        |
| 24                      | 163.9    | 1842.97    | 330.94                                 | -1.2891            | -1.2137        | -1.3406        | -1.8360        |
| 25                      | 166.7    | 2047.74    | 324.21                                 | -1.4216            | -1.3838        | -1.4554        | -1.9869        |
| 26                      | 169.4    | 2268.38    | 316.53                                 | -1.4001            | -1.4114        | -1.4177        | -1.9840        |
| 27                      | 172.2    | 2509.69    | 308.04                                 | -1.2963            | -1.3719        | -1.3024        | -1.9009        |
| 28                      | 175.0    | 2764.80    | 299.39                                 | -1.3611            | -1.5210        | -1.3659        | -1.9913        |
| 29                      | 177.8    | 3033.69    | 290.26                                 | -1.5740            | -1.8455        | -1.5972        | -2.2423        |
| 30                      | 180.6    | 3323.27    | 279.04                                 | -1.5115            | -1.9348        | -1.5895        | -2.2468        |
| 31                      | 183.3    | 3633.54    | 267.03                                 | -1.8484            | -2.4814        | -2.0502        | -2.7020        |
| 32                      | 186.1    | 3964.49    | 251.81                                 | -2.2763            | -3.2168        | -2.7448        | -3.3614        |
| <b>AAPD<sup>+</sup></b> |          |            |  | <b>0.9921</b>      | <b>0.9396</b>  | <b>1.0245</b>  | <b>1.2623</b>  |
| <b>APD<sup>++</sup></b> |          |            |  | <b>-0.9921</b>     | <b>-0.9396</b> | <b>-1.0245</b> | <b>-1.2619</b> |

\* Experimental data by (ASHRAE, 1989)

**\*\*** Dev% =  $100 \times (\rho_{cal} - \rho_{exp}) / (\rho_{exp})$ **+** AAPD =  $(100/\text{no. of points}) \sum_{i=1}^{\text{no. of points}} |\rho_{cal_i} - \rho_{exp_i}| / \rho_{exp_i}$ **++** APD =  $(100/\text{no. of points}) \sum_{i=1}^{\text{no. of points}} (\rho_{cal_i} - \rho_{exp_i}) / \rho_{exp_i}$ 

#### IV. CONCLUSIONS

Different methods have been evaluated for predicting the saturated liquid density of 5 synthetic liquefied natural gases as well as for pure methane. Six equations of state and four saturated liquid density correlations have been tested. Results indicate that the equation of state with temperature dependent co-volume parameter (NM EoS) can quite accurately predict the saturated liquid density of LNG mixtures to within 0.5% of experimental data. It seems that volume translation method applied to the SRK EoS does not improve greatly the accuracy of the SRK EoS for predicting the LNG density. Also, the results indicate that the SRK EoS itself is accurate enough for predicting the

saturated liquid density of LNG mixtures. As a matter of fact, it is well known that the SRK EoS is more accurate for light hydrocarbons (methane or methane-based mixtures), however, for heavy mixtures containing heptane, octane or their mixtures, the PR EoS exhibits better quality than the SRK EoS. Among the correlations, the NML predicts the saturated liquid densities of the LNG mixture with somewhat better quality than the HT and RSD correlations.

## Nomenclature

|          |   |
|----------|---|
| EOS      | equation of state                                 |
| $k_{ij}$ | binary interaction parameter                      |
| $N$      | no. of component                                  |
| $P$      | pressure, kPa                                     |
| $P_c$    | critical pressure, kPa                            |
| $P_r$    | reduced pressure                                  |
| $R$      | gas constant, 8.314 J/gr mole.K                   |
| $T$      | temperature, K                                    |
| $T_c$    | critical temperature, K                           |
| $T_r$    | reduced temperature                               |
| $V$      | molar volume, $m^3/gmole$                         |
| $V^*$    | pure component characteristic volume, $m^3/gmole$ |
| $x$      | mole fraction in liquid phase                     |
| $Z$      | compressibility factor                            |
| $Z_c$    | critical compressibility factor                   |
| $Z_c^*$  | critical compressibility parameter                |
| $Z_{RA}$ | improved compressibility factor                   |

## Greek Letters

|                |   |
|----------------|---|
| $\omega$       | acentric factor   |
| $\rho$         | density, $gmole/m^3$  |
| $\omega_{SRK}$ | optimized value of the acentric factor based on the SRK EOS |

## Subscript

|     |                      |
|-----|----------------------|
| cal | calculated value     |
| EOS | equation of state    |
| exp | experimental value   |
| i   | specie i             |
| j   | specie j             |
| mix | mixture              |
| s   | saturation condition |

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## APPENDIX

### Listing of equations and physical properties

**Table A1: The Soave-Redlich-Kwong [4] Equation of State (SRK EOS)**

|   |   |
|---|---|
| $P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$                     | $Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$   |
| $a_{C_i} = 0.42747 \frac{R^2 T_{C_i}^2}{P_{C_i}}$           | $b_i = 0.08667 \frac{RT_{C_i}}{P_{C_i}}$  |
| $m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$             | $\alpha_i^{0.5} = 1 + m_i(1 - T_r^{0.5})$   |
| $a_i = \alpha_{C_i} a_i$                                    | $a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i a_j} (1 - k_{ij})$                       |
| $b = \sum_{i=1}^N x_i b_i$                                  | $A = \frac{aP}{(RT)^2}, \quad B = \frac{bP}{RT} \quad \text{and} \quad Z = \frac{Pv}{RT}$ |
| <b>Volume Translated SRK</b>                                |   |
| $c_i = \frac{0.40768RT_{C_i}}{P_{C_i}} (0.29441 - Z_{RAi})$ | $c = \sum_{i=1}^N x_i c_i \quad \text{and} \quad V^L = V^{SRK} - c$                       |

**Table A2: The Peng-Robinson [3] Equation of State (PR EOS)**

|   |   |
|---|---|
| $P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2}$      | $Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0$  |
| $a_{c_i} = 0.45724 \frac{R^2 T_{c_i}^2}{P_{c_i}}$     | $b_i = 0.07780 \frac{RT_{c_i}}{P_{c_i}}$  |
| $m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$ | $\alpha_i^{0.5} = 1 + m_i(1 - T_r^{0.5})$   |
| $a_i = \alpha_{c_i} \alpha_i$                         | $a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i a_j} (1 - k_{ij})$                       |
| $b = \sum_{i=1}^N x_i b_i$                            | $A = \frac{aP}{(RT)^2}, \quad B = \frac{bP}{RT} \quad \text{and} \quad Z = \frac{Pv}{RT}$ |

**Table A3: Critical Point and Physical Properties used in this Work**

| Comp.            | $T_c$ ,<br>K | $P_c$ ,<br>bar | $MW$   | $\omega$ | $Z_c$ | $V_c$ ,<br>L/mole |
|------------------|--------------|----------------|--------|----------|-------|-------------------|
| C <sub>1</sub>   | 190.56       | 45.990         | 16.043 | 0.011    | 0.289 | 0.0986            |
| C <sub>2</sub>   | 305.33       | 48.714         | 30.070 | 0.099    | 0.285 | 0.1455            |
| C <sub>3</sub>   | 369.83       | 42.480         | 44.097 | 0.152    | 0.277 | 0.2000            |
| i-C <sub>4</sub> | 407.85       | 36.400         | 58.124 | 0.186    | 0.283 | 0.2627            |
| n-C <sub>4</sub> | 425.10       | 37.960         | 58.124 | 0.200    | 0.274 | 0.250             |
| i-C <sub>5</sub> | 460.39       | 33.810         | 72.151 | 0.229    | 0.268 | 0.3083            |
| n-C <sub>5</sub> | 469.70       | 33.700         | 72.151 | 0.252    | 0.269 | 0.3110            |
| N <sub>2</sub>   | 126.20       | 33.980         | 28.014 | 0.037    | 0.291 | 0.0910            |

**Table A4: Correlation Parameters used in this Work**

| Comp.            | C <sub>1</sub> | C <sub>2</sub> | C <sub>3</sub> | $\delta_{S-NML}$<br>$\times 10^2$ | $\delta_{NML}$<br>$\times 10^2$ | $\omega_{SRK}$ | $V^*$<br>L/mole | $Z_c^*$ | $Z_{RA}$ |
|------------------|----------------|----------------|----------------|-----------------------------------|---------------------------------|----------------|-----------------|---------|----------|
| C <sub>1</sub>   | 0.5857         | -0.7206        | 1.2899         | -3.20525                          | -3.17189                        | 0.0074         | 0.0994          | 0.3321  | 0.2892   |
| C <sub>2</sub>   | 0.7178         | -0.7644        | 1.6396         | -1.46429                          | -1.57101                        | 0.0983         | 0.1458          | 0.3281  | 0.2807   |
| C <sub>3</sub>   | 0.7647         | -0.6111        | 1.3958         | -0.25595                          | 0.59160                         | 0.1532         | 0.2001          | 0.3220  | 0.2767   |
| i-C <sub>4</sub> | 0.8288         | -0.8285        | 2.3201         | 3.10327                           | 2.58999                         | 0.1825         | 0.2568          | 0.3247  | 0.2749   |
| n-C <sub>4</sub> | 0.8787         | -0.9399        | 2.2666         | 0.13196                           | 1.38194                         | 0.2008         | 0.2544          | 0.3239  | 0.2732   |
| i-C <sub>5</sub> | 0.9767         | -0.6043        | 1.4025         | 0.09888                           | 0.14613                         | 0.2400         | 0.3069          | 0.3245  | 0.2720   |
| n-C <sub>5</sub> | 0.9820         | -1.1695        | 2.7523         | 0.62738                           | 0.42676                         | 0.2522         | 0.3113          | 0.3223  | 0.2686   |
| N <sub>2</sub>   | 0.5867         | -0.4459        | 0.8926         | -0.79463                          | -0.86475                        | 0.0358         | 0.0901          | 0.3350  | 0.2895   |