Technical Note

On the Non-Ideality of Hydrocarbon Fluids: Implications for Natural Gas Engineering – Part B

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Abstract

This work presents a unified treatment of non-ideality that ties together the ubiquitous concepts of compressibility factor, Joule-Thomson coefficient, fugacity coefficient, and fugacity that are routinely used in natural gas engineering. The development is based on the identification of common misconceptions and the construction of a unified approach for the analysis of non-ideality. Starting with the basic ideal equation of state, an integrated treatment is progressively built in which the concept of non-ideality is thoroughly reviewed and its implications for natural gas engineering extensively discussed. The treatment of non-ideality given here is unique in scope and non existent in the available natural gas engineering literature. In the second part of this series, the implications of the non-ideality for natural gas engineering are reviewed and discussed.

Introduction

In the first part of this series[1], a graphical interpretation of the concept of Z-factor and fugacity coefficient was presented. The compressibility factor (Z) was presented as a *volumetric multiplier* that, when applied to an ideal EOS prediction, was capable of generating real fluid volumetric data. The fugacity coefficient (ϕ) was presented as the thermodynamic property that measures non-ideality as a function of the magnitude of the area between curves generated by the lack of compliance between real volumetric data and ideal predictions.

The introduction of "Z" in our engineering calculations is based on our need of extending the applicability of the all-convenient ideal equation of state even for conditions of pressure and temperature where the ideal model is not applicable. The concept of compressibility factor can then be presented as the ratio of actual fluid volume to ideal volume predicted by the ideal EOS, as shown below:

$$Z = \frac{v_{real}}{v_{ideal}}, \qquad \text{........(1)}$$

which is just a reinforcement of of the idea that Z operates as a multiplier to v_{ideal} that generates v_{real}. When "*v*" refers to the real, experimental value of molar volume at the given pressure and temperature, the fact that Z just acts as a multiplier that forces the ideal volumetric prediction (RT/p) to generate actual experimental values of molar volume generates the following equation:

$$Z \cdot \left(\frac{RT}{p} \right) = v \qquad \text{...........(2)}$$

Or,

$$Z \equiv \frac{pv}{RT} \qquad \text{...........(3)}$$

Equation 3 is usually given as the definition of the compressibility factor. Equation 3 can be written to resemble the ideal EOS, as follows:

$$pv = ZRT\,, \qquad \text{...........(4)}$$

which is the omnipresent equation used in gas engineering calculations (i.e, the "real gas" equation of state). In this paper, the implications of non-ideality in terms of compressibility inversion, energetic inversion, and liquid/vapor equilibrium are analyzed.

Implications of Non-ideality: The Compressibility Inversion

Figure 1 displays the behavior of the compressibility factor (Z) with respect to pressure and temperature. Figure 1 was generated using real volumetric data for methane as predicted by the popular Peng-Robinson EOS[2]—a cubic EOS. Cubic EOSs are based on van der Waals ideas, the first physicist to introduce meaningful pressure and volume corrections to the ideal model and who enunciated the principle of the corresponding states (PCS). According to the PCS, all fluids have the same compressibility factor when they are found at corresponding states. Two fluids are said to be in corresponding states when they have same reduced conditions (i.e., same p_r, T_r, and same acentric factor, for the case of the three-parameter PCS). Most hydrocarbons and thus natural gases would then reveal approximately the same volumetric behavior, in terms of Z, shown in Figure 1 as long as the appropriate reduced conditions are considered.

Figure 1 shows a useful p-T mapping of iso-Z lines for a variety of conditions of pressure and temperature. Regions where "Z" takes the value of one (or close to one) constitute all possible combinations of pressure and temperature for which the ideal EOS generates reliable volumetric predictions. This region is highlighted in dark grey in Figure 1. Since liquid-solid transitions are not predicted by the Peng Robinson EOS (or any other cubic EOS for that matter), the solid region and solid/liquid line presented in Figure 1 has been superimposed on the figure based on the methane experimental data compiled by IUPAC[3]. The predicted vapor/liquid transition or vapor pressure curve (which starts at the triple point and ends at the critical point p_r=T_r=1) is also highlighted. The lower end of the vapor pressure curve (methane's triple point) is found at p_r=0.0025 and T_r=0.4759, a condition which cannot be predicted by cubic EOSs. It should be noted that any cubic EOS would still generate liquid volumetric values for the region $T_r < Tr_{triple}$, where no liquid is present.

If all conditions found to the right of the vapor pressure curve are considered "gaseous" states, it would become clear that the smallest gas Z-factors (i.e., the largest deviations from ideality) are found around the critical point conditions ($p_r = T_r = 1$). Cubic EOSs predict the same *critical* compressibility factor (Zc, Z at p_r=T_r=1) for all fluids—which is a direct consequence of the principle of corresponding states. As Figure 1 indicates, the Peng Robinson EOS predicts a universal $Z_c = 0.307$ for all fluids. In reality, Z_c–values are not exactly the same for all fluids and they range between 0.23 and 0.31. For methane, Z_c is actually equal to 0.2863. On the other hand, the region where minimum deviations from ideality take place, i.e., the region where fluid volumetric behavior is exactly predicted by the ideal EOS (Z=1) and its vicinity ($0.99 < Z < 1.01$), is shown in grey in Figure 1. The figure corroborates that fluids can be said to behave "ideally" at low pressures (i.e., $p_r < 0.25$, regardless of temperature) and at high temperatures if pressures are not too high. It should be noted that for pressures $p_r >> 7$, Z-factors are always greater than one, which indicates that the ideal model would consistently underpredict volume at those conditions.

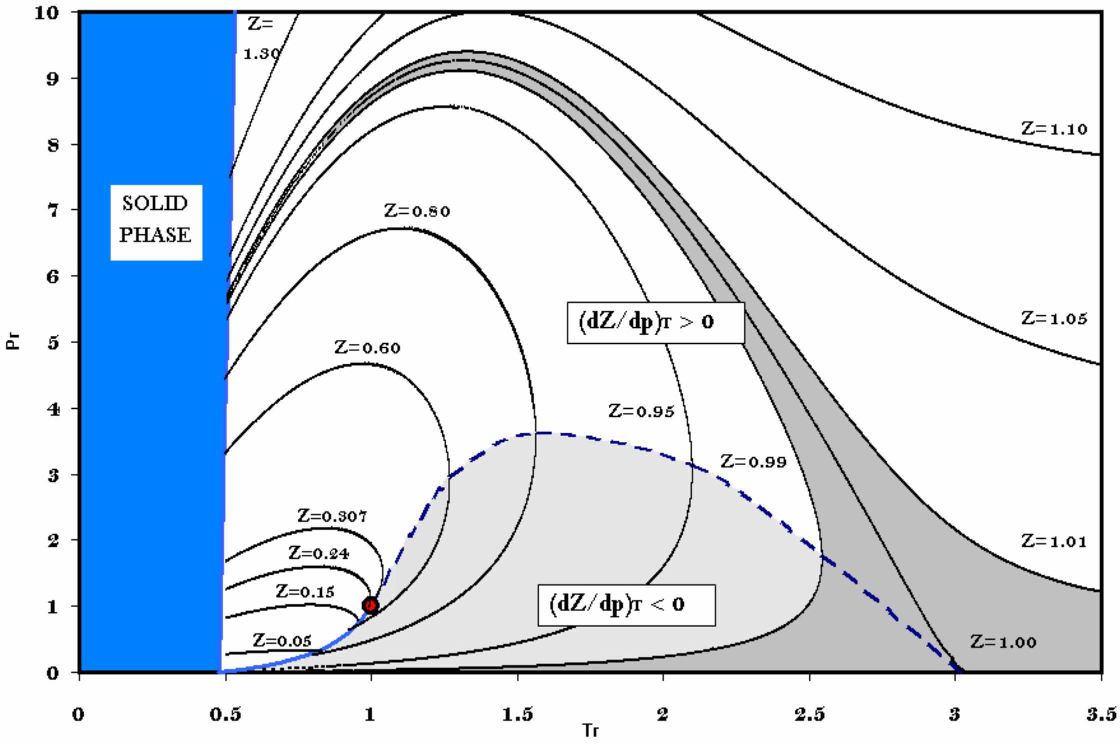

Figure 1: Non-Ideality in the p-T plane: the compressibility inversion

Liquid states, found to the left of the critical point and above vapor pressure conditions, have compressibility factors that can range from Z=0.01 or below (at low pressures and temperatures) up to Z=1.50 or more (at high pressures). It is important to indicate that liquids can indeed exhibit compressibility factors equal to one (Z=1). Note that Z=1 isoline extends well into the liquid region and up to the solid/liquid transition. As discussed in the preceding article of this series[1], this has little to do with the fluid behaving ideally at those conditions but is rather the consequence of repulsion forces dominating the behavior of the liquid. Cubic EOSs, such as the one used to generate Figure 1, are also known for generating poor liquid density predictions (i.e., poor Z-factor predictions for liquids). However, they are capable of reproducing a good qualitative prediction of volumetric behavior, which is the main interest of this work.

The close resemblance between the names *compressibility factor*—Z, a measure of non-ideality—and *isothermal compressibility factor*—c_f, the measure of the relative change of volume of a fluid with changes in pressure at constant temperature—may be seen as unfortunate but it is justified. The term *compressibility* represents the ability of a fluid be compressed or the degree to which a fluid can undergo a reduction in volume under pressure. Even though the compressibility factor (Z) *does not* measure this type of compressibility, it does *control* it. This can be better elucidated by recalling that Z-factor and fluid isothermal compressibility (c_g) are related through the equation:

$$c_f = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = c_g\Big|_{ideal} - \frac{1}{Z}\left(\frac{\partial Z}{\partial p}\right)_T$$

$$\text{where} \quad c_g\Big|_{ideal} = \frac{1}{p} \qquad \text{.........(5)}$$

Equation 5 demonstrates that whether a fluid is more easily compressed than its ideal counterpart depends on the sign of $(dZ/dp)_T$. Fluids are more easily compressed than their ideal counterpart when $c_f > c_{g(ideal)}$, which occurs when $(dZ/dp)_T$ is negative. Fluids with $c_f < c_{g(ideal)}$ are less compressible than their ideal counterpart, and a positive $(dZ/dp)_T$ would be an indicator of that. Therefore, the condition $(dZ/dp)_T=0$ defines what could be defined as a *compressibility inversion curve*, shown in Figure 1 with a broken line. Under most conditions of interest (inside the compressibility inversion curve), natural gases are *more* compressible than their ideal counterparts. Outside of the inversion curve, fluids are less compressible than their ideal counterpart at the same pressure and temperature condition. For instance, ideal gases will compress to a third of their volume when the confining pressure is tripled (Boyle's law), but this would not be true for real gases. In reality, natural gases are found to be *more* compressible than what the ideal model would predict. The use of *compressibility* factors can effectively correct this compression discrepancy, as indicated below:

$$\text{If } \frac{p_2}{p_1} = 3 \rightarrow \frac{v_2}{v_1} = \frac{1}{3} \cdot \frac{Z_2}{Z_1}$$

(at constant temperature) ....(6)

Equation 6 shows that the volume of a *real* gas will, in fact, decrease to less than one-third of the original volume as long as $Z_2/Z_1 < 1$, which is the case when the isothermal compression takes place inside the inversion curve. Inside the inversion curve, attraction forces dominate molecular behavior and will effectively act to shrink the fluid to a volume smaller than what is predicted by the ideal model. Outside the compressibility inversion curve, repulsion forces start counteracting attraction forces and the fluid would not shrink as much ($Z_2/Z_1 > 1$). It is important to indicate that the compressibility inversion curve represents the locus of all minimum Z's that show up in typical Z vs. p charts. In a typical Z vs. p chart (e.g., see Figures 6 and 7 in Ref. 1), isotherms start at Z=1 at p=0 and then take values Z <1 with increasing pressure [$(dZ/dp)_T < 0$] up to the point of compressibility inversion [where $(dZ/dp)_T = 0$]. At pressures higher than the compressibility inversion pressure, Z increases with increasing pressure [$(dZ/dp)_T > 0$]. Note that at temperatures $T_r > 3$, compressibility inversion does no longer exist for those isotherms (i.e., $(dZ/dp)_T$ is always positive).

Figure 2 displays lines of constant isothermal compressibility values, calculated via equation 5 using the data presented in Figure 1. Isothermal compressibility values are given in reduced units ($c_r = p_c * c_f$). It is evident in this figure that fluid compressibility is a strong function of pressure and temperature, and that it takes its largest values in the low-pressure gas region and its smallest values in the liquid region. Vapors right below the vapor pressure curve represent the most compressible state of a substance. It is evident that the vapor pressure curve marks a sharp discontinuity in the compressibility values and behavior of a substance. In addition, Figure 2 shows that liquid compressibility is a weak function of pressure. That justifies the traditional approach of assuming liquids to have an approximately constant c_f within reasonable pressure ranges—the basis of the "slightly compressible fluid" model used in numerical simulation. It should be noted, however, that liquid compressibility is a strong function of temperature. And while fluid compressibility tends to increase with temperature for all fluids outside the compressibility inversion curve, compressibility tends to decrease with temperature inside the inversion curve. In addition, the iso-c_r lines are rather flat in regions of low pressure and high temperature. At such conditions, fluids behave near ideally and the compressibility is thus independent of temperature.

Typical c_r's for reservoir natural gases ranges between 0.1 and 1.0. Compressibility is an important property in natural gas engineering. The behavior of fluid volume with pressure is key in the transient analysis and modeling of oil and natural gas engineering systems. For example, fluid compressibility is one of the fluid properties that control the speed at which a pressure disturbance will propagate through a hydrocarbon reservoir, an important consideration in the field of pressure transient analysis. Compressibility behavior is also a paramount consideration in the design of handling facilities. In this section, it has been established that the derivative $(dZ/dp)_T$ is instrumental for the description of the compressibility behavior of fluids and the definition of the compressibility inversion curve. When a fluid (such as a liquid or high pressure gas) is found outside the compressibility inversion curve, it becomes less compressible than its ideal reference and its compressibility becomes much more sensitive to temperature changes and increases with temperature. Fluids inside the inversion curve are more compressible than ideal gases and their compressibility decreases with temperature.

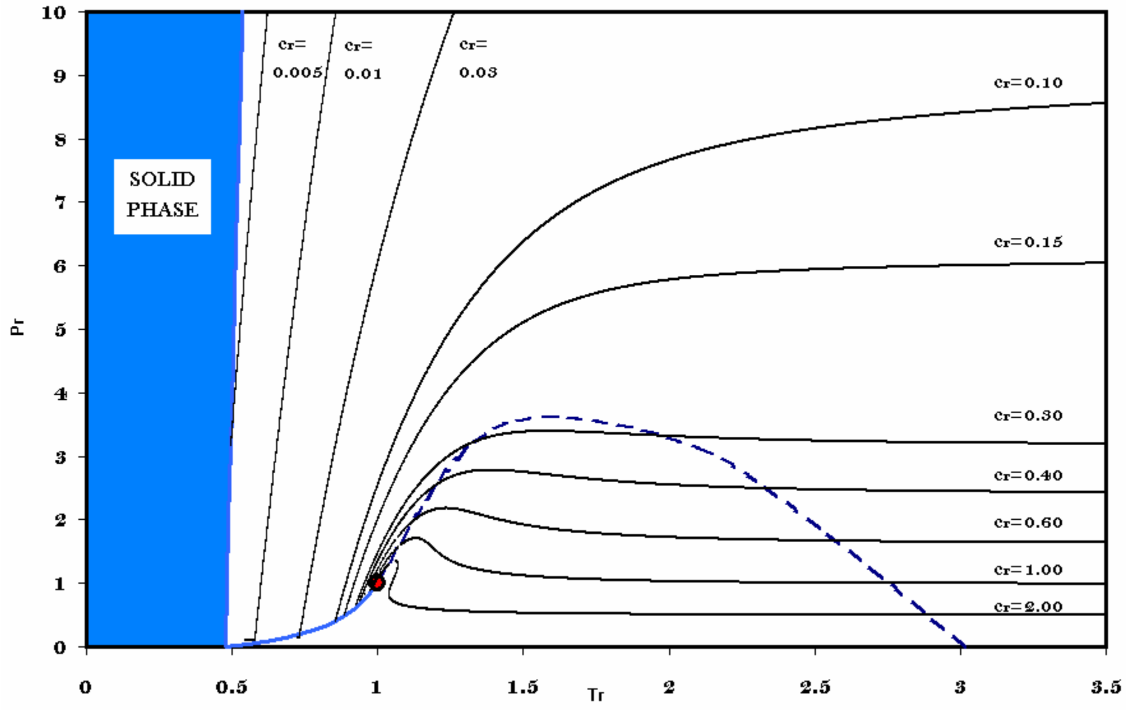

Figure 2: Lines of constant isothermal compressibility

Implications of Non-ideality: The Energetic Inversion

Figure 3 takes a second look at the Z-factor data generated by the Peng-Robinson EOS for the case of methane. In this section, it is demonstrated that the concept of non-ideality (measured via Z-values) not only controls the behavior of fluid compressibility, but also effectively describes their energetic behavior. One key concept in the description of energetic behavior is the *Joule-Thomson coefficient*. The *Joule-Thomson coefficient* (μ) is the mathematical measure of the effect of pressure drop on temperature during throttling or isenthalpic expansions. The effect of throttling has a number of important applications in natural gas engineering and the temperature change that results of letting a fluid freely expand from a higher to a lower pressure is frequently called the *Joule-Thomson effect*. The Joule-Thomson coefficient is thermodynamically related to Z-factor through the following expression:

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h = \frac{RT^2}{pc_p}\left(\frac{\partial Z}{\partial T}\right)_p \qquad ....(7)$$

where c_p = constant pressure heat capacity. Since c_p is never zero, equation 7 shows that the condition $(\partial Z/\partial T)p = 0$ is sufficient to define the condition $\mu = 0$ or energetic inversion locus. And because all terms other than the Z-factor derivative are always positive, equation 7 also shows that the sign of the Joule-Thomson coefficient directly depends on the sign of $(\partial Z/\partial T)p$. All transition points where $(dZ/dT)_p$ takes a zero value define the *energetic inversion curve* depicted in Figure 3. Cooling occurs when μ (i.e., dZ/dT) is positive—i.e., inside the inversion envelope—and heating occurs when μ (i.e., dZ/dT) is negative—i.e., outside the inversion envelope.

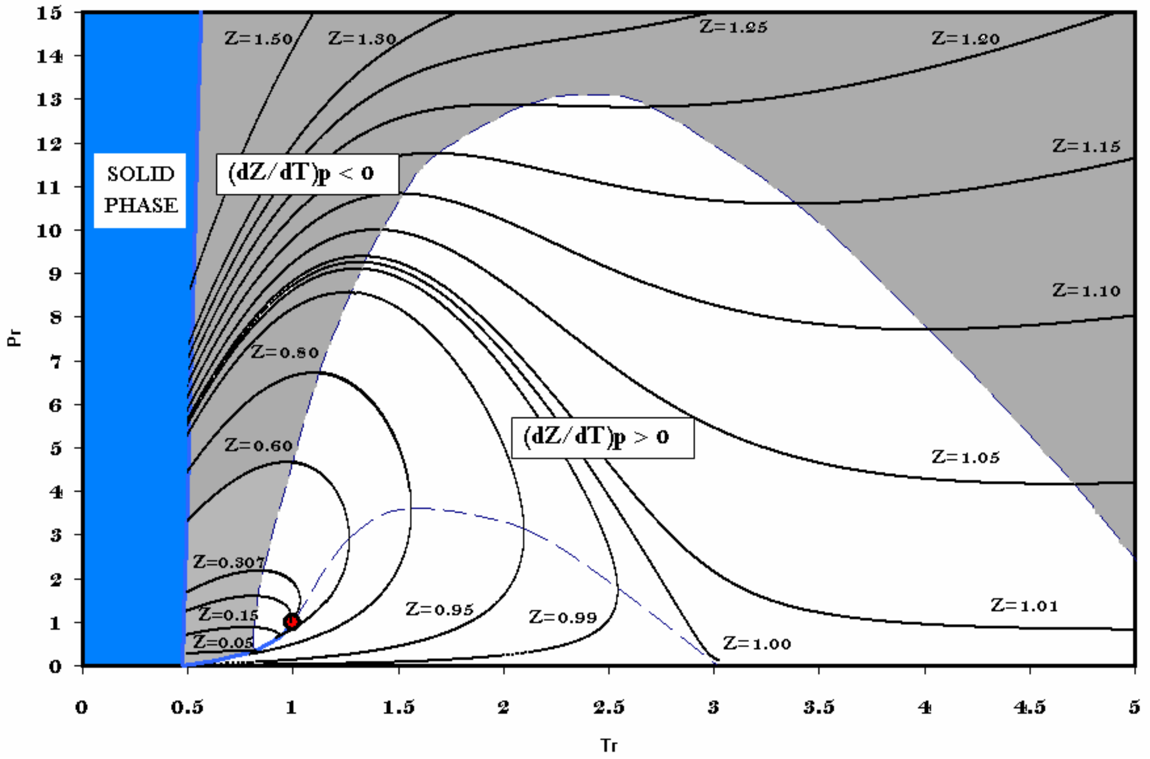

Figure 3: Non-Ideality in the p-T plane: the energetic inversion

In the previous section, $(dZ/dp)_T$ effectively defined a compressibility inversion curve. Figure 3 demonstrates that the derivative $(dZ/dT)_p$ also defines a new boundary that marks an important change in the thermodynamic behavior of natural gases. This behavior of Z with temperature has significant implications for the thermodynamics of natural gases. As discussed above, when the term $(dZ/dT)_p$ is positive (i.e, the fluid is found at conditions inside the energetic inversion curve in Figure 3), the free expansion of the fluid would lead to its cooling—such as what happens when natural gas enters separators or when it crosses chokes or valves. Natural gases typically reduce their temperature when they undergo adiabatic expansion, and this is controlled by the behavior of the derivative $(dZ/dT)_p$. When $(dZ/dT)_p$ is negative, such expansion would result in an increase of fluid temperature instead. Natural gases are known to cool upon isenthalpic expansion, and this fact is commonly used in the production of LNG (liquid methane). The reduction in fluid temperature needed in natural gas liquefaction systems is typically achieved by *throttling*—the isenthalpic process of changing the temperature of a fluid by adiabatic expansion. For cooling upon isenthalpic expansion to be possible, the non-ideal behavior of the natural gas fluid has to be such that $(dZ/dT)_p$ should take a positive value within the region of operation.

Ideal gases do not change their temperature upon throttling. Even though the "ideal region" for this fluid (grey region in Figure 1) is contained inside the inversion envelope, truly ideal gases neither cool nor heat upon isenthalpic expansion because dZ/dT is identically zero for ideal gases (i.e., Z=1 at all conditions). Real fluids *approach* such behavior at high temperatures ($T_r > 3$) and pressures below $p_r = 10$, because iso-Z curves are approximately flat and changes in Z with temperature become much less significant (see Figure 3). In summary, fluids found within the left "half" of the inversion curve (close to the critical point of the fluid) will experience much larger temperature drops during throttling—such as when natural gases expand into separators or at chokes in wellheads—than fluids found within the "right" half of the inversion dome. It should be noted that the energetic inversion curve completely encloses the compressibility inversion curve because it extends through a much larger area in the p-T plane. Therefore, it is concluded that all fluids that are more compressible than their ideal counterparts will always cool upon isenthalpic expansion. The location of both inversion curves should be regarded as approximate, since different equations of state would predict slightly different locations for both curves.

An important realization that should be visualized in Figure 3 is that liquids have p-v-T properties that cause them to rise in temperature when they are expanded adiabatically, while gases usually show the opposite effect. Liquid systems typically operate above the vapor-pressure curve and below critical conditions, *i.e.*, within the region that is found to the left and outside of the inversion curve. Therefore, liquid hydrocarbon systems would typically heat upon adiabatic expansion—because $(dZ/dT)_p$ is negative for such conditions. In contrast, most natural gas systems operate at $T_r > 1$ and inside the inversion curve, and consequently their volumetric behavior $[(dZ/dT)_p > 0]$ would cause them to drop their temperature upon adiabatic expansion (i.e., "Joule-Thomson cooling"). The transition from cooling to heating, represented by the inversion envelope, starts around $0.80 < T_r < 0.90$ and can be used to distinguish liquid-like from gas-like thermodynamic behavior when fluids are single phase, especially around critical conditions ($p_r = T_r = 1$).

Fugacity and non-ideality

The previous two sections have shown that the concept of non-ideality, and even more importantly, non-ideality changes with pressure and temperature $[(dZ/dT)_p$ and $(dZ/dp)_T]$ are the cornerstones of a true understanding of fluid behavior in natural gas engineering. Another important concept for the understanding of the implications of non-ideality in natural gas engineering is that of fugacity and fugacity coefficient. **Figure 4** maps the behavior of fugacity coefficient with pressure and temperature, based on the predictions of "v_{real}" generated for methane using the Peng-Robinson EOS and the definition of fugacity coefficient given in equation 8 and discussed in part A of this series[1]:

$$RT\ln\phi = \int_0^p \left[v - v_{ideal}\right]dp$$

@ a given temperature ……….(8)

It can be corroborated in Figure 4 that at the lower end of the integration range ($p_r \rightarrow 0$), all fugacity coefficients are equal to one. For most pressures and $T_r < 2$, fugacity coefficients are smaller than one ($\phi < 1$), which indicates that real volumetric isotherms (v_{real}) are mostly found to left of the ideal isotherm (v_{ideal}) at such conditions. At high temperatures ($T_r > 3$), fugacity coefficients are larger than one because, as already seen in Figure 1 and 3, the ideal model tends to underpredict real data ($Z > 1$) at those conditions.

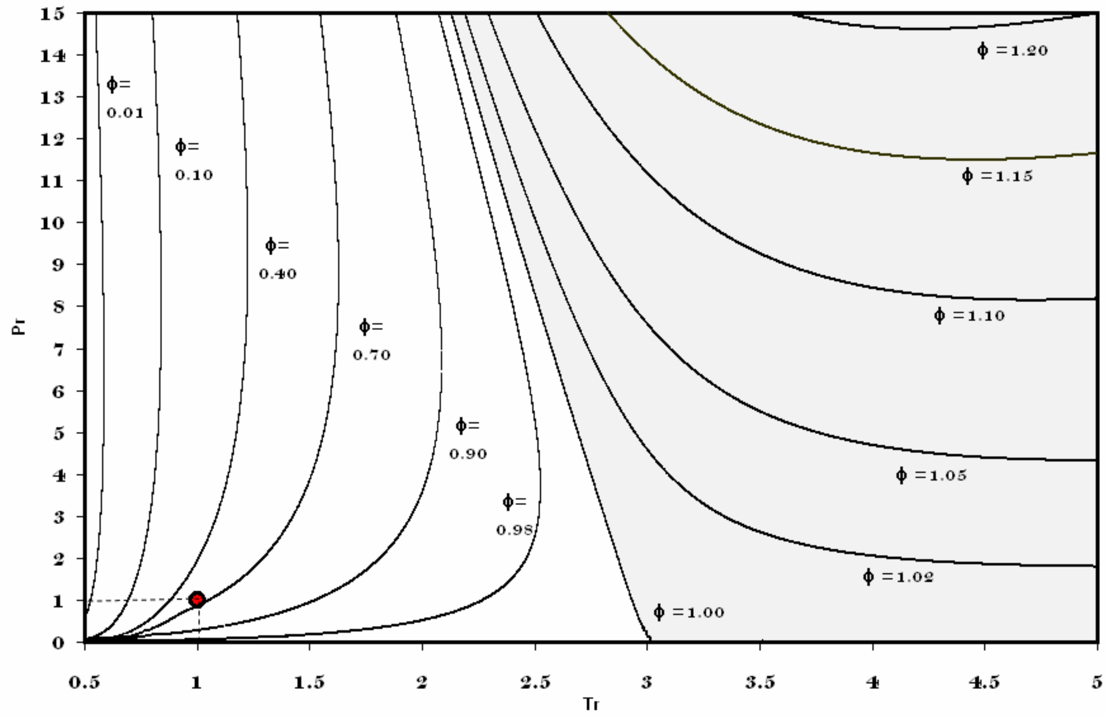

Figure 4: Methane fugacity coefficient in the p-T plane

For pure substances, fugacity coefficient is related to *fugacity* through the following ratio:

$$\phi = \frac{f}{p} \qquad \text{…………(9)}$$

As a consequence of this definition, fugacity is looked upon as a modified pressure since equation (8) can be rearranged to show that:

$$f = p \cdot EXP\left\{ \frac{1}{RT} \int_0^p [v_{real} - v_{ideal}] dp \right\}$$

@ const T ………...(10)

Fugacity characterizes the escaping tendency of the molecules from one phase to the other. Fugacities and chemical potentials *are* the driving forces for mass transfer between two phases. In the heart of it, fugacity is a representation of the Gibbs free energy of a fluid. For pure substances, fugacity and Gibbs free energy are related through the expression:

$$dG = RTd \ln f \qquad \text{@ const T} \qquad \text{………...(11)}$$

with $\lim_{p \to 0} f = p$.

This expression constitutes the equation by which fugacity is defined and related to all other energetic properties of the fluid. Thermodynamic equilibrium requires both phases to have the same Gibbs free energy, and such requirement implies that the fugacities of both phases are equal. For multicomponent mixtures, each component has a value of fugacity that can be associated to it, per phase, and that will controls its movement (mass transfer) between the two phases. For instance, when the fugacity of methane is higher in the liquid than it is in the gas, methane will transfer (vaporize) to the vapor phase. Mass transfer will stop when there are no longer any driving forces for mass transfer.

Fugacity is a powerful tool in thermodynamics and it is the key tool utilized in the prediction of phase equilibrium both for pure substances and complex mixtures in natural gas engineering. Many natural gas engineering applications operate on hydrocarbon phase behavior principles. Analysis of separation equipment, multiphase flow in natural gas reservoirs, wellbores and pipelines, LNG and NGL processing, LNG tankers, and natural gas storage is based on phase behavior principles. Take, for example, the case of methane liquefaction operations. **Figure 5** presents a mapping of the values of fugacity coefficient of methane, as predicted by the Peng-Robinson EOS, around the conditions of methane liquefaction conditions (methane vapor pressure curve). The location of the liquid/vapor transition in Figure 5 was delineated using the concept of fugacity and fugacity coefficient discussed above, which is entirely based on volumetric data. The methane liquefaction line is identified as the line where the fugacity of the liquid and the fugacity of gas are identical. A notorious change in slope of the iso-ϕ lines also helps the identification of the vapor pressure line. It should be noted that even though both Z and ϕ measure departure from non-ideality, their behavior along the vapor/liquid co-existence region is quite distinct. Z is used to generate density values, and ϕ is used to generate fugacity values. On the one hand, two co-existing phases along the vapor pressure curve must have different Z-factor values because both phases have different densities. This density difference will obviously disappear as the critical point is approached. On the other hand, two co-existing phases along the vapor pressure curve must have the same fugacity coefficients, because both phases must have the same fugacity at all points of the vapor pressure curve.

Liquefaction of methane is an important industrial process that produces LNG (liquefied natural gas)—the liquefied version of methane at ultralow temperatures or about 110 K at atmospheric pressure. Transportation of natural gas across the oceans requires its transformation to a condensed form (LNG) that can minimize volume storage requirements. What is commonly done to liquefy gaseous methane is to compress it to a high pressure, cool it at constant pressure to a low temperature, and then expand it to a low pressure and even lower temperature through a Joule-Thomson expansion in order to cause its liquefaction. LNG operations are the prime example in natural gas engineering where the concepts of non-ideality, Z-factor, Joule-Thomson effect, and liquid-vapor phase behavior concepts are brought together under the same umbrella. All these concepts have been discussed in this paper and it has been shown that all of them have their roots in the non-ideal behavior of natural gases.

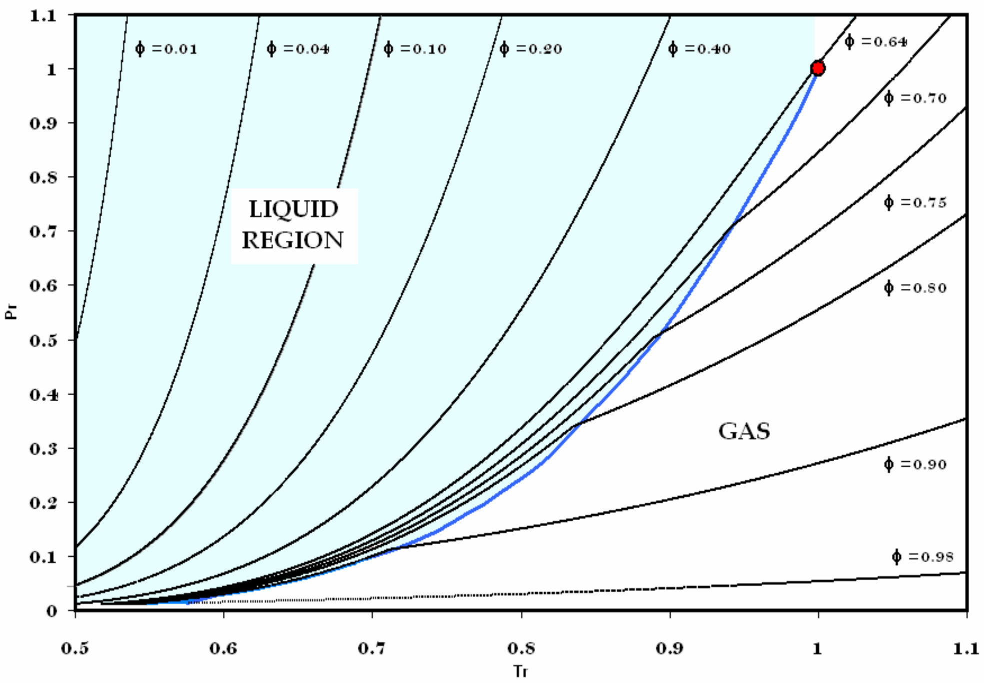

Figure 5: Fugacity coefficient and the gas/liquid transition region

Concluding Remarks

In this two-article series, the concepts of non-ideality, Z-factor, Joule-Thomson coefficient, and fugacity, have been analyzed and extensively reviewed. Hydrocarbon phase behavior deals with the analysis of oil and gas engineering systems, in which hydrocarbon fluids undergo many property-altering intermediate stages. Understanding of fluid phase behavior—i.e., the volumetric behavior of all possible fluid phases as a function of pressure, temperature, and composition—is essential for optimal design and safe and efficient operation of engineering systems dealing with fluids. Using *ideal* behavior as the benchmark behavior of reference, this study has proposed a unified approach for the analysis of non-ideality and its implications for many applications in natural gas engineering.

Nomenclature

c_f = fluid's isothermal compressibility (Pa^{-1})
c_r = fluid's reduced isothermal compressibility (dimensionless)
f = fugacity (Mpa)
G = Gibbs free energy (KJ/mol)
p = pressure (Mpa)
p_c = critical pressure (Mpa)
p_r = reduced pressure (dimensionless)
R = gas universal constant (R = 8.314 cm^3 Mpa/mol-K)
T = temperature (K)
T_c = critical temperature (K)
T_r = reduced temperature (dimensionless)
v = molar volume (cm^3/mol)
Z = compressibility factor (dimensionless)
Z_c = critical compressibility factor (dimensionless)
ϕ = fugacity coefficient (dimensionless)
μ = Joule Thomson coefficient (K/MPa)

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