Technical Note

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

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Abstract

This work presents a unified treatment of non-ideality that uniquely ties the concepts of compressibility factor, Joule-Thomson coefficient, fugacity coefficient, and fugacity, that are routinely used in natural gas engineering. This 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 part A of this two-article series, the concepts of fluid compressibility factor (Z) and fugacity coefficient (ϕ) are reviewed, and a unique graphical interpretation for both is presented.

Introduction

The concept of compressibility factor (Z) is the most ubiquitous concept in the myriad of engineering applications that deal with fluid phases—gases in special. Gas engineering design equations that do not utilize compressibility factor "Z" values are extremely scarce. The behavior of compressibility factor with pressure, extensively published in form of graphs in all engineering books and manuals (see, for example, Ref. 1 to 7), is usually presented without major discussion about the significance of shapes and trends within the graph, while it is plainly stated that "Z" is a fluid property that measures non-ideality or corrects for non-ideality. For instance, the very idea that that the value of "Z" is equal to *one* for ideal gases is widely accepted, but the notion that a fluid can have a compressibility factor "Z" equal to one but yet not being ideal is very often overlooked. Some additional confusion is brought upon by the close resemblance between the names *compressibility factor*—a measure of volumetric deviance of the ideal gas model with respect to experimentally measured data—and *isothermal compressibility factor*—the latter being the measure of the relative change of volume of a fluid with changes in pressure at constant temperature. To circumvent this difficulty, some authors prefer referring to "Z" as the *compression factor*[8], which might be a more proper name for it, but the widespread preference for the usage of the name "*compressibility factor*" is indisputable. Another valuable measurement of non-ideality is the concept of *fugacity coefficient*, which is a property that is much less commonly used to measure non-ideality unless liquid-vapor applications are of interest. In this study, a graphical interpretation of the Z-factor and fugacity coefficient concepts is presented. Both concepts are interrelated and the development is used as the basic for the analysis of non-ideal phenomena of interest in natural gas engineering.

The Failure of the Ideal Model

The ideal gas law,

$$pv = RT \, , \qquad \ldots\ldots..(1)$$

is a simple, clean, straight-forward, and unpretentious equation that describes the relationship among pressure (p), temperature (T), and molar volume (v) for a special kind of fluid: the "ideal" type. This equation, however, has great limitations when it comes to predicting fluid volumetric behavior within a wide range of pressure and temperature conditions. An *ideal gas* is an imaginary fluid that satisfies, among few others, the following two characteristics: (a) *interactions among its molecules are non-existent, and (b) molecular volume is negligible (with respect to total volume occupied by the fluid).* When assumptions (a) and (b) describe the molecular dynamics of a fluid, Statistical Thermodynamics demonstrates that equation 1 can describe the p-v-T behavior of the substance. Naturally, the validity of assumptions (a) and (b) stated above has a great impact on the actual predictive ability of equation 1.

Figure 1 presents the hyperbolic compression paths predicted by the ideal EOS for the isothermal compression of methane at three different temperatures of interest (T_r=0.80, 1.00, and 2.00). These hyperbolic paths are known as Boyle's isotherms, and they plainly indicate that the volume of an ideal gas is inversely proportional to its pressure. Different temperatures generate different hyperbolic paths, with the concavity of the hyperbola decreasing with increasing temperature. Data are presented in terms of reduced conditions of pressure, temperature, and volume in order to facilitate the extension of this discussion to any other fluid of interest. Reduced conditions employ critical conditions of the fluid (p_c, T_c, v_c) as scaling factors of *p, T, and v* such that:

$$p_r = \frac{p}{p_c} \quad ; \quad T_r = \frac{T}{T_c} \quad ; \quad v_r = \frac{v}{v_c} \qquad \ldots\ldots(2)$$

For methane[9], p_c = 4.5992 MPa, T_c = 190.564 K, and v_c= 98.628 cm^3/mol. By virtue of the principle of corresponding states, fluid volumetric behavior of other various substances follow similar paths in terms of reduced conditions. Using the principle of corresponding states, volumetric behavior presented in this paper can be used to predict behavior of a variety of substances by employing the appropriate critical values.

It is important to note that there are at least two troublesome features in the ideal isotherms presented in Figure 1 that constitute, nevertheless, reasonable consequences of the ideal assumptions (a) and (b) previously stated. Those are: **i)** In the ideal model, volume vanishes along the high pressure asymptote ($v \to 0$ as $p \to \infty$). In reality, molecules *do* have volume and they *cannot* be forced too closely together without triggering molecular repulsion. There exists a minimum non-zero volume (known as the co-volume) that substances maintain when subjected to a large pressures, which is the result of the finite, non-zero volume of their molecules and the strength of the repulsion forces. In short, the volume of a real substance cannot and will not vanish at high pressures. **ii)** The ideal model cannot predict phase transitions, i.e., the ideal model cannot predict the condensation of the compressed gas into a liquid phase. Such condensation transitions appear in p-v diagrams in the form of sharp discontinuities that are obviously absent in Figure 1. When compression of a pure gaseous fluid takes place at temperatures below the critical (T_r < 1), the gaseous phase eventually condenses into a liquid phase. **Figure 2** displays the p-T vapor pressure curve for a real gas (methane), where it is shown that a vapor-liquid transition must occur during the isothermal compression of the gas at T_r = 0.80 (subcritical conditions). Figure 1 demonstrates that the ideal model fails predicting such transition, given that the subcritical isotherm for T_r=0.80 does not show any discontinuity and just behaves as the other two but with a different concavity. In summary, and since molecular volume and interaction is ignored in the ideal model, ideal gases vanish in volume at high pressures and cannot and will not condense regardless of temperature.

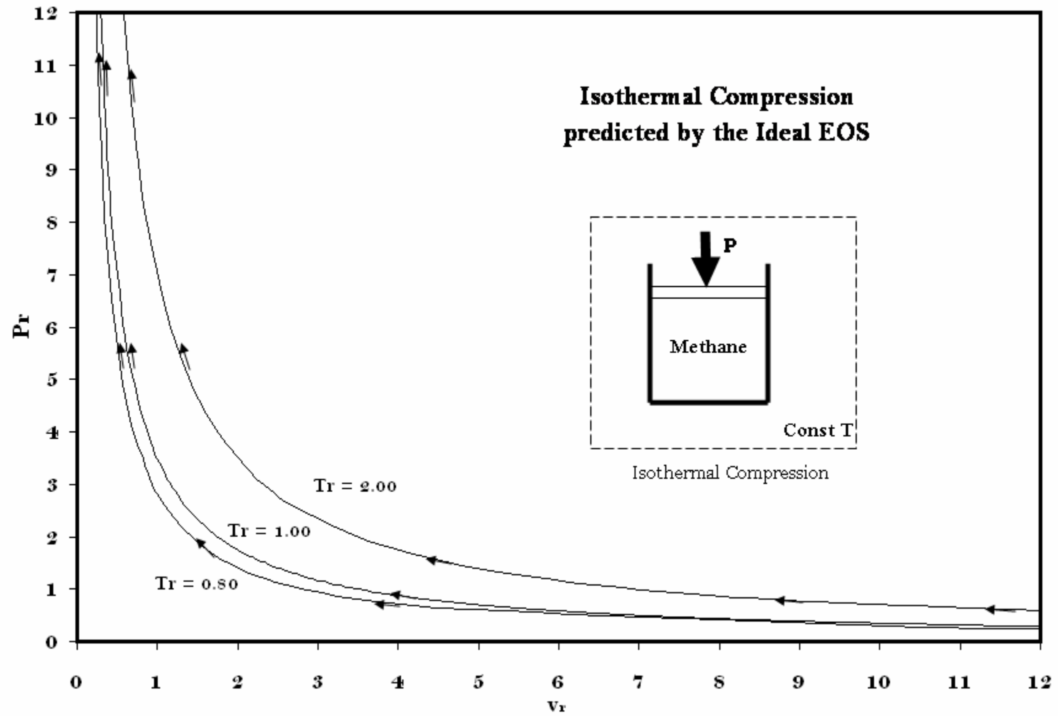

Fig. 1: Isothermal compression of ideal gases

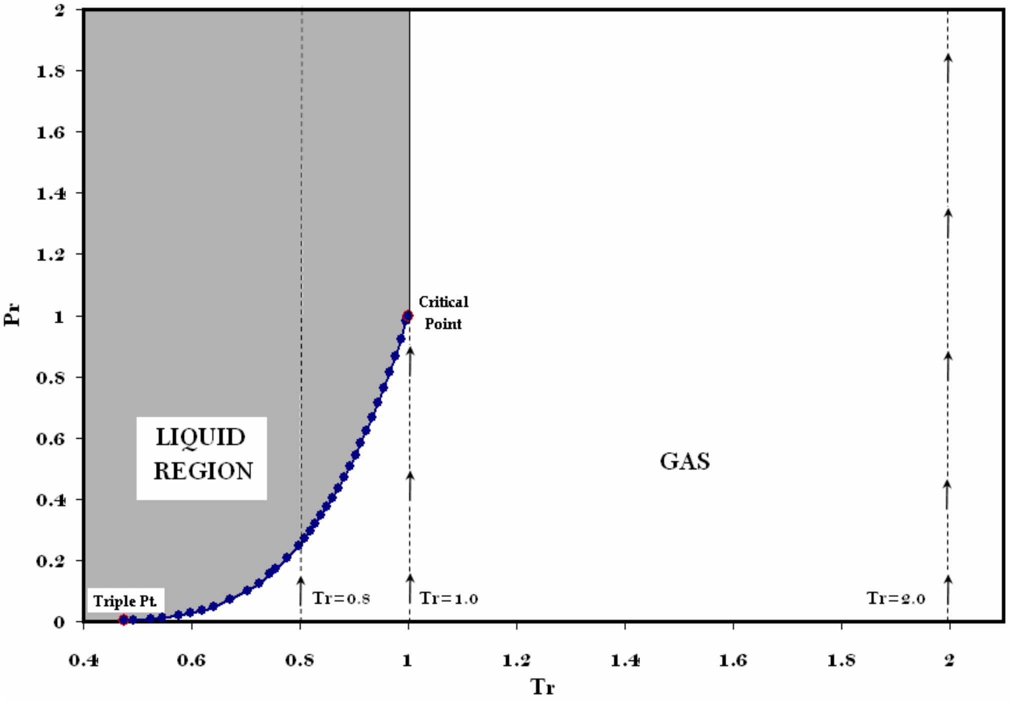

Fig. 2: Methane vapor pressure curve

Figure 3 shows experimental p-v-T data for methane for the conditions of interest. Experimental p-v-T data for methane used in this paper has been taken from the IUPAC International Thermodynamic Tables[9]. **Figure 4** presents a detail of the same experimental p-v-T data around the phase transition region at condensation conditions. For comparison purposes, ideal predictions have been superimposed in these figures. The shaded areas in **Figure 3** and **4** clearly confirm that the ideal model is qualitatively incorrect in terms of shapes and trends and quantitatively incorrect in terms of actual prediction values—especially at low temperatures ($T_r \le 1.0$). These shaded areas represent the key indicator that the ideal model is, indeed, quite uncapable of generating reliable fluid volumetric behavior data within the range of pressure and temperature conditions being considered.

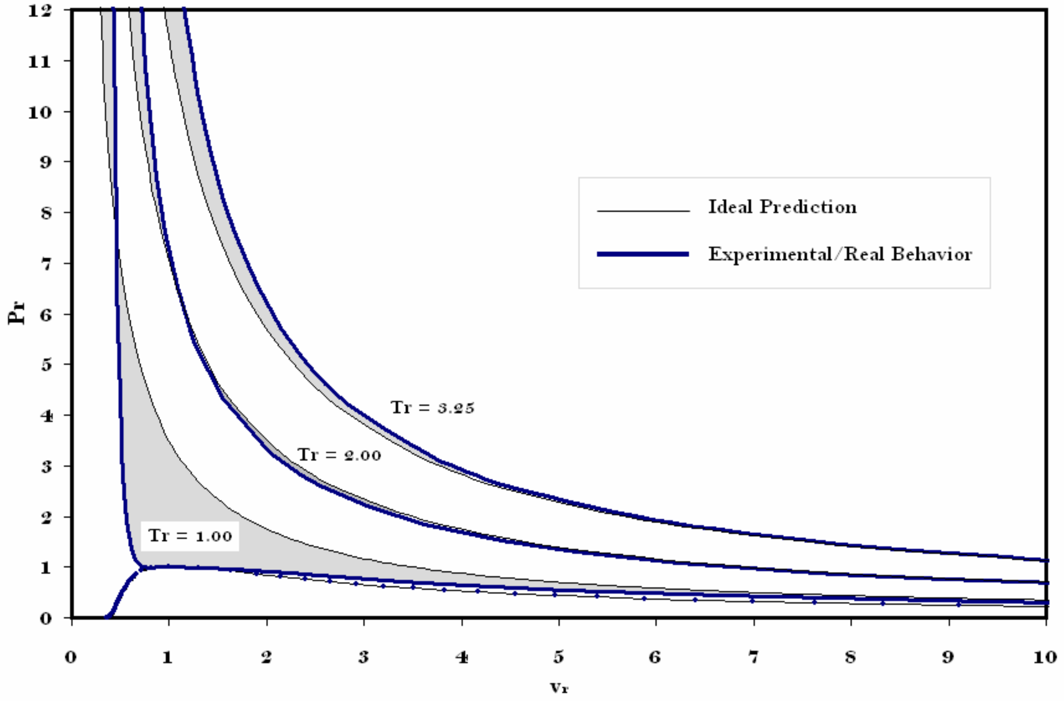

Fig. 3: Methane volumetric behavior: Ideal vs. Experimental T_r = 1, 2, 3.25

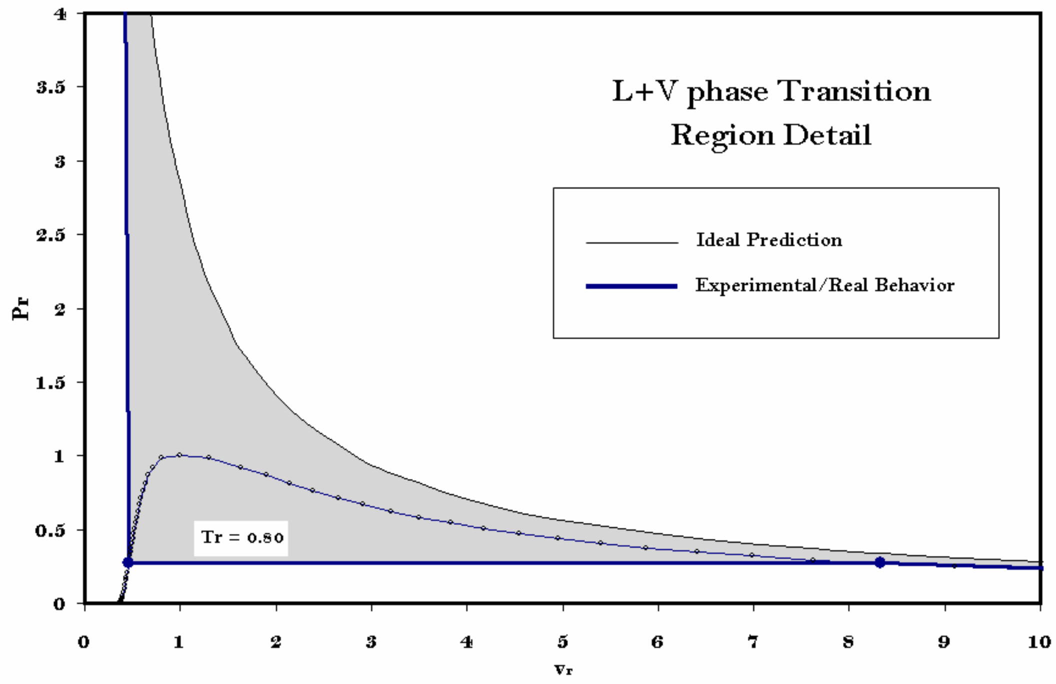

Fig. 4: Methane volumetric behavior: Ideal vs. Experimental T_r = 0.80

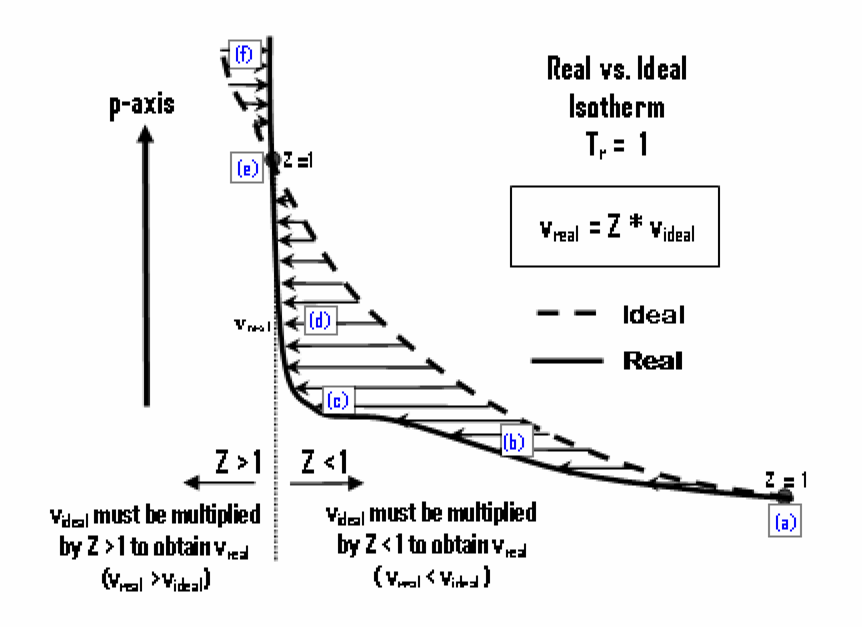

Fig. 5: Definition of Z as a volumetric correction factor

A Volumetric Correction for the Ideal EOS: A Graphical Interpretation

An important realization, often overlooked when dealing with Z-factor calculations, is that compressibility factor values are point-by-point volumetric corrections that seek to eliminate the shaded areas in Figure 3 and 4 in such a way that ideal isotherms are literally forced to collapse on top of real isotherms. In other words, Z-factors are *pressure-dependent multipliers* that, when applied to the ideal EOS isotherms in Figure 3 and 4, would generate the experimental/real volumetric isotherms shown in the same figures. **Figure 5** demonstrates that such a multiplier would necessarily take different values at different pressures. For the purposes of the discussion depicted in Figure 5, only the ideal and real critical isotherms (T_r = 1) is considered.

In Figure 5, the multiplier "Z" is visualized as the number that, when applied to the ideal prediction, generates the real value ($v_{real} = Z * v_{ideal}$). In this figure, it is demonstrated that the volumetric correction factor "Z" takes different values at different pressures because the volumetric departure of the ideal EOS with respect to real data ("$v_{real} - v_{ideal}$") is dependent on pressure. Based on this figure, several observations ("a" to "f", identified along the isotherm) can be made about the behavior of "Z" with increasing pressure, an abridged list of which is discussed hereunder. These observations on Figure 5, letters *a* through *f,* can be summarized as:

a. At low pressures, the ideal model approaches the real behavior and the multiplier "Z" takes the value of unity (Z = 1).

b. As pressure increases, the ideal model starts overpredicting volume ($v_{ideal} > v_{real}$) and the multiplier becomes Z < 1. Since $v_{real} < v_{ideal}$, then Z < 1 because $v_{real} = Z * v_{ideal}$. The value of the multiplier "Z" keeps decreasing with increased pressure within this region because the volumetric departure "$v_{real} - v_{ideal}$" increases with pressure.

c. The value of the multiplier "Z" reaches a minimum value at the condition where the volumetric deviation "$v_{real} - v_{ideal}$" is greatest. In the case of the critical isotherm (T_r=1), this maximum volumetric deviation (minimum Z) occurs close to critical point conditions.

d. After a minimum value of "Z" is attained (corresponding to the maximum volumetric deviation), the gap "$v_{real} - v_{ideal}$" starts to narrow if pressure is further increased. The value of the multiplier "Z" starts to increase along with pressure, maintaining a value of less than unity and approaching it.

e. At very large pressures, the two isotherms eventually intercept and "Z" regains the value of unity Z=1, for the second time in this description.

f. After regaining the value of one, the Z-multiplier starts taking values of larger than one (Z > 1) when pressure continues to increase. Within this region, the ideal model consistently underpredicts volume ($v_{real} > v_{ideal}$) and hence Z > 1. It should be noted that the ideal isotherm tends to go to zero ($v_{ideal} \to 0$ as $p \to \infty$) but the real isotherm (v_{real}) maintains a rather constant value with a close-to-vertical slope. "Z" keeps increasing as $p \to \infty$ because v_{ideal} keeps approaching zero as pressure increases while v_{real} maintains an approximately constant value because of repulsion forces.

In summary, **Z** is, simply stated, a number or a *volumetric multiplier* that, applied to an ideal EOS prediction, is capable of generating reliable fluid volumetric data. The introduction of "Z" in our engineering calculations is based on our need of retaining 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 previously described behavior of the multiplier "Z" with pressure, for the given isotherm, can be summarized by plotting these trends in a graph of *Z* versus pressure, as shown in **Figure 6**. As seen in Figure 6 and discussed in Figure 5, "Z" would take the value of one at low pressures and becomes Z < 1 as pressure is increased. At some point, "Z" reaches a minimum (for the critical isotherm, this point is found close to the critical point or p_r=1) and then increases with along with pressure until it reaches a value of Z=1 (around 7 < p_r < 8) and keeps increasing as Z > 1 thereafter. The Z vs. p chart presented in Figure 6 can be extended to any other isotherm of interest: using the information available in Figures 3 and 4 and implementing the concept of "Z" as a volumetric multiplier, a more complete version of the *Z-p* chart is generated and presented in **Figure 7**. Both Figure 6 and 7 present, using a discontinuous line, the values of "Z" associated to each of the saturated liquid and saturated vapor line (i.e., the liquid-vapor phase boundary) shown in Figure 4.

The reason why "Z" becomes one at large pressures should be carefully examined. This has very little to do with the assumptions of the ideal model becoming valid at high pressures. At this point (typically found at $p_r > 7$), the fluid is far removed from the ideal assumptions since molecular interactions are very strong and cannot be neglected. The reason why "Z" becomes one ($Z=1$) is because of the crossover of isotherms that takes place at high pressures (observation ***e***). The reason behind the isotherm crossover is that pressure and molecular closeness are significant and repulsion forces dominate and prevent further shrinkage and additional molecular closeness (liquid-like behavior). The slope of the real isotherm becomes close to vertical while the ideal model crosses over taking the ideal volume prediction to zero. As a result, a value of $Z=1$ can only be used as the *definition* of ideality if it is implied that Z must remain equal to one with changes in pressure and temperature (it should be noted that, at the point of the isotherm crossover, changes in pressure or temperature will make Z take values $\neq 1$). Values of $Z < 1$ are the norm for most pressure conditions of interest, but at values of pressure far removed from criticality ($p > 7\ p_c$), Z can take values higher than 1, indicating the presence of liquid-like (nearly constant volume) behavior. In short, all ideal fluids exhibit $Z=1$, but the reverse is not always true.

Figure 6 also shows that all isotherms converge to $Z=1$ at low pressure conditions, regardless of temperature. The qualifier "low pressure" is largely dependent on the particular substance and its own critical pressure, typically pressures below $p < 0.25\ p_c$. For gases, the smallest value of compressibility factor is usually found around $0.2 < Z < 0.3$. For the critical isotherm, the smallest Z factor is found in the neighborhood of the critical point, where the largest volumetric deviations from ideal-gas behavior take place. For methane[2], $Z_c = 0.2863$. For most fluids, the critical compressibility (Z at $p_r=T_r=1$) is found within the range 0.23 to 0.31. Z-factors are lower than one whenever attractive forces operate to reduce the volume of the fluid below of that of an equal amount of ideal gas; and this occurs below the point of isotherm crossover found at pressures greater than seven times p_c where $Z=1$. At large pressures ($p_r > 7$), however, repulsive forces will prevail and the volume of the real fluid cannot be able to be reduced to that of an equal amount of ideal gas (therefore, $Z > 1$).

At high temperatures ($T_r > 2$), Z factors hovers around unity, regardless of pressure and as long pressure is not larger than $p_r > 7$. This corroborates the generalization or rule of thumb that says that gases behave ideally *at low pressures and high temperatures*, which are the conditions at which the ideal assumptions are largely valid. For subcritical conditions ($T_r < 1$), discontinuities must be expected in Z vs. p plots around saturation conditions. Discontinuities do occur at pressure values equal to the vapor pressure of the substance at the temperature of interest. Under such conditions (e.g., $T_r = 0.80$ in Figures 4 and 7), a liquid+vapor transition takes place at constant pressure and two different values of Z-factor are associated with the two-phase fluid: one corresponding to the liquid phase and another corresponding to the gas phase. Liquid compressibility factors are used to calculated liquid densities, and their values are typically smaller than those of critical compressibility ($Z < 0.30$). Liquid compressibility factors are commonly computed, along with vapor compressibility factors, during liquid-vapor equilibrium calculations.

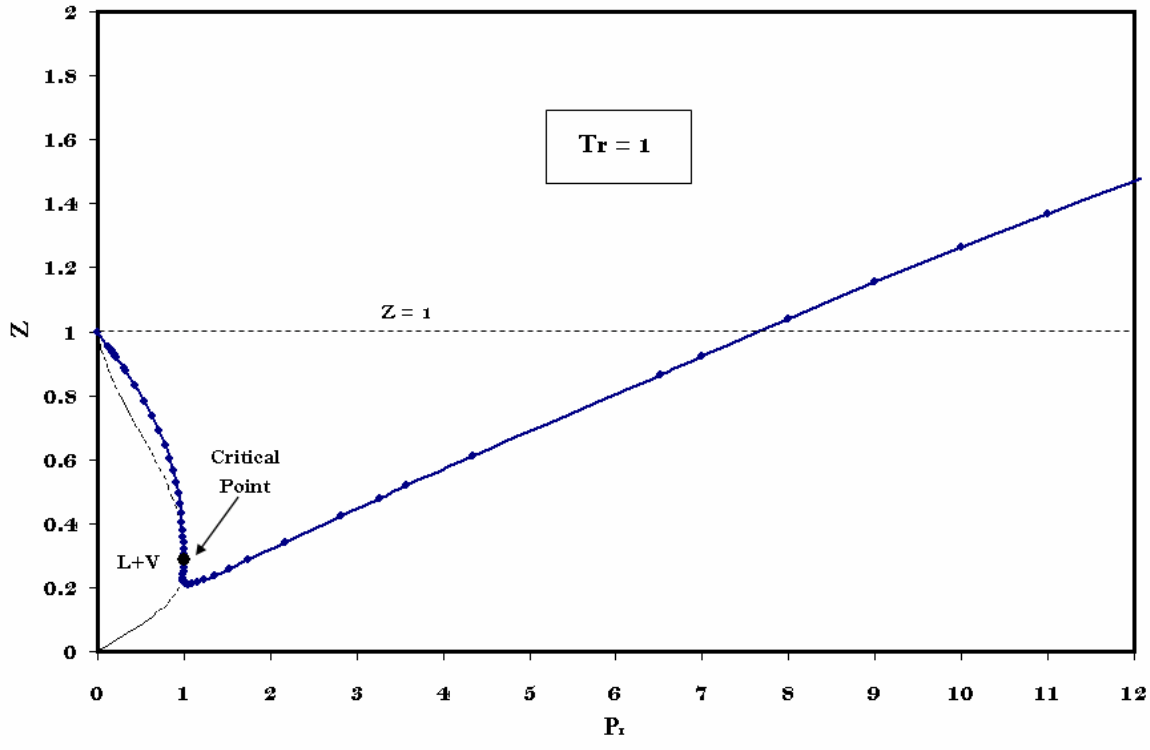

Fig. 6: Behavior of the *Z*- multiplier with pressure, T_r = 1

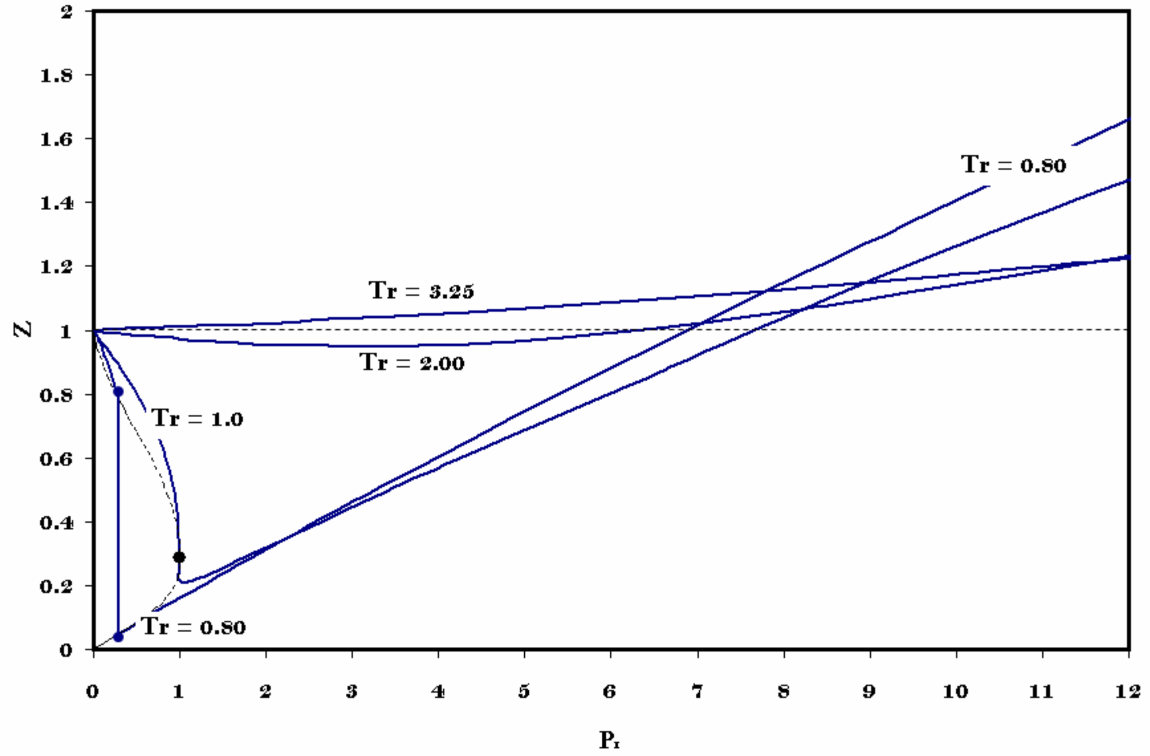

Fig. 7: Behavior of the Z-factor with pressure at different temperatures

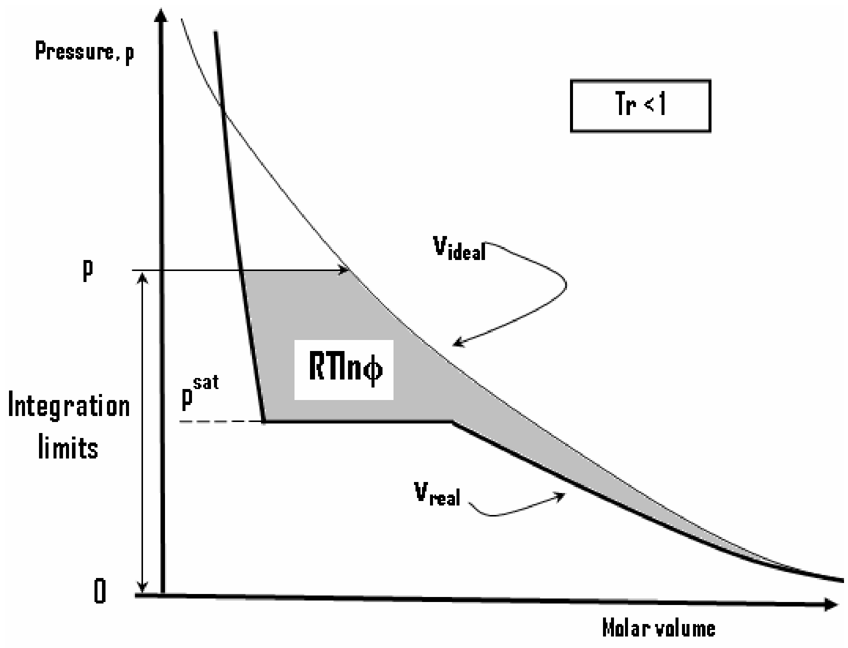

Fig. 8: Non-Ideality and the concept of fugacity coefficient

Non-ideality and Fugacity Coefficient

In lieu of using the concept of Z-factor, the lack of compliance of the ideal isotherm with respect to experimental measurements could be quantified in a different way. **Figure 8** shows that the volumetric deviation between the ideal isotherm (v_{ideal}) and real isotherm (v_{real}) could also be expressed in terms of the magnitude of the *area between the two curves* (shaded area). Such a property, that would measure non-ideality in terms of the *area of lack-of-compliance* between ideal and real isotherms, would also be a pressure-dependent property because the size of this area would change for different pressure levels. For such a property, ideality would be realized when both isotherms were to be found on top of each other, i.e., when the area in between isotherms becomes non-existent.

The *fugacity coefficient* concept is the thermodynamic property that utilizes the shaded area in Figure 8 in order to quantify non-ideality. Fugacity coefficients (ϕ) are calculated by integrating the volumetric deviation between the real data and ideal prediction, for a given temperature, between a low pressure (where ideality can be assumed) and a pressure of interest, as follows:

$$RT \ln \phi = \int_0^p \left[v - v_{ideal} \right] dp$$
$$\text{@ a given temperature} \qquad \ldots(3)$$

When both isotherms in Figure 8 are found on top of each other, $RT\ln\phi = 0$, thus $\phi = 1$ and the fluid is regarded ideal. By the same token, if the area to the left of the ideal isotherm were equal to the area to the right, $\ln\phi = 0$ and $\phi = 1$. Fugacity coefficient then becomes another effective way of assessing non-ideality. **Figure 9** shows the calculation of fugacity coefficient with pressure for the isotherms $T_r = 0.80$, 1.00, 2.00, and 3.25 considered in Figures 3 and 4. At the lower end of the integration range ($p \rightarrow 0$), 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 7, the ideal model tends to underpredict real data ($Z > 1$) at those conditions.

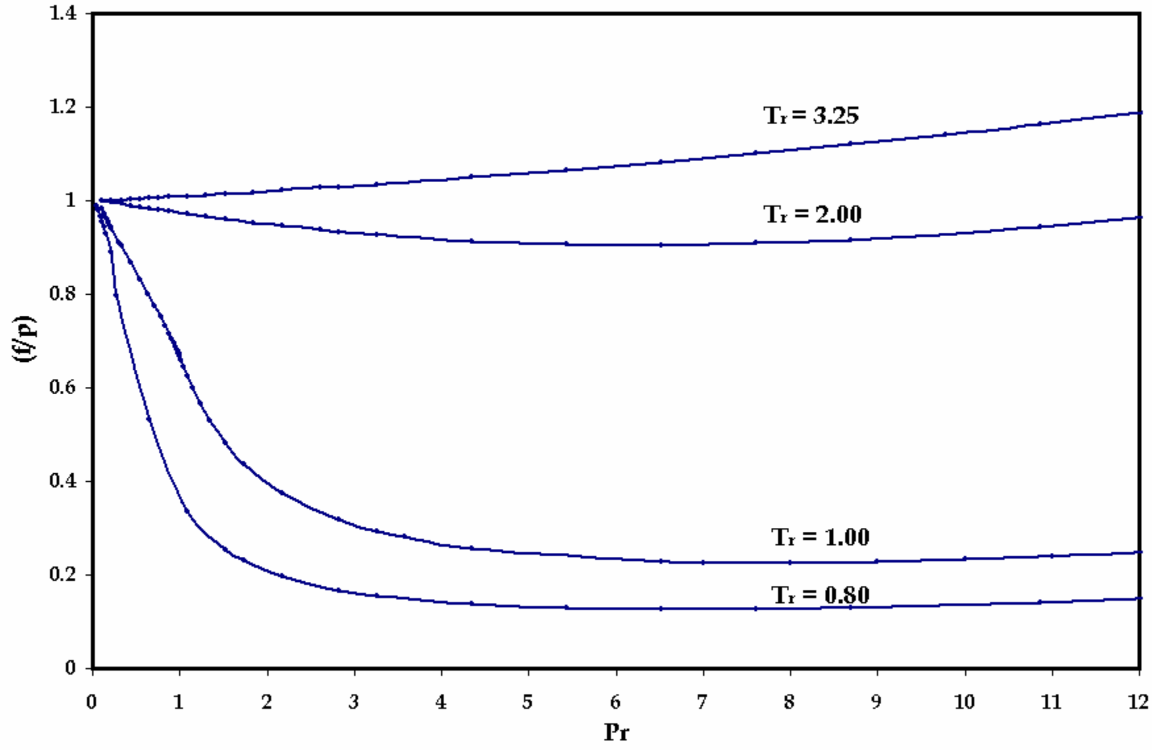

Fig. 9: Behavior of fugacity coefficient versus pressure for methane

Z-factors and fugacity coefficients, both measures of non-ideality, can be easily related through equation (4), which is the result of substituting the definitions $v = Z \cdot v_{ideal}$ and $v_{ideal} = \frac{RT}{p}$ into equation (3):

$$\ln \phi = \int_0^p \left[\frac{Z-1}{p} \right] dp \quad \text{@ constant T} \qquad \ldots\ldots..(4)$$

It is important to note that, although related, the concepts of "*Z*" and "ϕ" provide two different yardsticks to measure non-ideality. While Z-factors provide point-by-point quantification of the deviation "v_{real} - v_{ideal}" as a function of pressure, fugacity coefficients quantify the behavior of "v_{real} - v_{ideal}" within the region bounded by *p=0* and the pressure of interest.

Fugacity coefficients are calculated in applications involving fugacity computations. For pure substances, fugacity coefficient is related to *fugacity* through the following ratio:

$$\phi = \frac{f}{p} \qquad \ldots(5)$$

As a consequence of this definition, fugacity is looked upon as a modified pressure since equation (5) can be rearranged to show that:

$$f = p \cdot EXP\left\{ \frac{1}{RT} \int_0^p \left[v_{real} - v_{ideal} \right] dp \right\} \quad \text{@ const T} \qquad \ldots(6)$$

It is a basic thermodynamic premise that two pure phases in equilibrium have the same fugacity. It is important to corroborate that this is indeed the case at the horizontal liquid/vapor transition or constant pressure line found at p^{sat} in Figure 8. Both the saturated liquid and the saturated vapor found at the two ends of the horizontal liquid/vapor transition have the same fugacity and fugacity coefficient, despite of having two very distinct densities and Z-factors, because both conditions yield the same identical area between the real and ideal isotherms within the interval $0 < p < p^{sat}$. Fugacity then becomes one of the most important thermodynamic properties used in the prediction of co-existence of two or more phases—a quality that will be elaborated upon in part B of this series. In addition, it should be noted, through Equation 6, that fugacity of an ideal gas equals its pressure because $v_{real}=v_{ideal}$ for such conditions.

Concluding Remarks

In this work, the author presents a unique and meaningful graphical interpretation of non-ideality through the concepts of compressibility factor and fugacity coefficient. The delineated step-by-step analysis of the concept of the compressibility factor (Z) and fugacity coefficient (ϕ) proves to be an eye-opener to engineers dealing with natural gases, especially when it comes to understanding the behavior of Z with pressure and the concept of non-ideality at large. Thermodynamic and fluid behavior literature never fails to present *Z and ϕ vs. p* charts; but the reasons behind the trends observed in those charts usually remain obscure. In Part B of this two-article analysis[10], the implications of non-ideal behavior for natural gas engineering will be examined based on the development described in this paper. The concepts of compressibility inversion, Joule-Thomson effects, and fugacity, and their relation to non-ideality, will be then thoroughly discussed.

Nomenclature

f = fugacity (Mpa)
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)
v_c = critical volume (cm^3/mol)
v_r = reduced temperature (dimensionless)
Z = compressibility factor (dimensionless)
Z_c = critical compressibility factor (dimensionless)
ϕ = fugacity coefficient (dimensionless)

References

1. Smith, J.M., Van Ness, H.C., and Abbott, M. **Introduction to Chemical Engineering Thermodynamics**, 7th edition, McGraw Hill, pp. 64-109, 2005.
2. Çengel, Y.A., and Boles, M.A. **Thermodynamics: An Engineering Approach**, 5th edition, McGraw Hill, pp. 139-143, 2006.
3. Sandler, S. I. **Chemical and Engineering Thermodynamics**, 3rd edition, John Wiley & Sons, Inc, pp. 225-238, 1999.
4. Gas Processors Suppliers Association, *GPSA Engineering Data Book*, 12th Edition, Section 23, pp. 10-17, Tulsa, OK, 2004.
5. Guo, B., and Ghalambor, A., **Natural Gas Engineering Handbook**, Gulf Publishing Company, pp. 20-25, 2005.
6. Whitson, C.H., and Brule, M.R. **Phase Behavior**, SPE Monograph v. 20, Henry L. Doherty Series, Richardson, TX, pp. 22-24, 2000.
7. Danesh, A. **PVT and Phase Behaviour of Petroleum Reservoir Fluids**, *Developments in Petroleum Science* v. 47, Elsevier, pp. 79-85, 2001.
8. McNaught, A. D. **IUPAC Compendium of Chemical Terminology**, 2nd Edition, Blackwell Science, 1997.
9. Wagner, W., and K.M. de Reuck. **International Thermodynamic Tables of the Fluid State**—*v. 13: Methane*. **IUPAC Chemical Data Series**, Blackwell Science, pp. 135-337, 1996.
10. Ayala, L., **On the Non-Ideality of Hydrocarbon Fluids: Implications for Natural Gas Engineering – Part B**, e-journal of reservoir engineering, v.1, n.1, Nov. 2006.