General Friction Theory Viscosity Model for the PC-SAFT Equation of State

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In this work, a general f-theory viscosity model based on the perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state (EoS) has been developed for the description of the viscosity behavior of the normal alkanes family (from methane to n-octadecane). This general f-theory model has been shown to provide satisfactory results for the modeling of the viscosity of the normal alkanes as well as carbon dioxide and nitrogen over wide ranges of temperatures and up to 100 MPa. In addition, using simple mixing rules, an evaluation of the model performance has been carried out for several n-alkane and carbon dioxide + n-alkane mixtures over wide ranges of temperature and pressure. The chosen mixing rules provide good mixture viscosity prediction, close to or within experimental uncertainty, which is satisfactory for most applications (industrial and research). Further, the combination of the PC-SAFT EoS with the f-theory adds one more thermophysical property to the list of properties for which this model already delivers an improved representation, making the application potential for the PC-SAFT EoS even wider. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 1600–1610, 2006

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Introduction

Within a wide range of engineering disciplines, viscosity is an important fluid property required in a large number of applications such as the design of transport equipment, the simulation of chemical processes, the simulation of petroleum reservoirs, the blending and transportation of oil and gas, lubrication, and refrigeration. In most of these applications, the pressure and temperature dependencies of the viscosity are critical parameters. In some cases, such as the production of deep-water petroleum reservoirs, a reservoir fluid can go from high-pressure and high-temperature conditions to ambient conditions, which would necessarily imply phase separation and important compositional variations. Consequently, reliable and accurate viscosity models are in increasing demand for applications covering everyday wider and more extreme ranges of temperature, pressure, and composition. Thus, multiproperty models capable of providing accurate description not only of a fluid's phase and volumetric behavior but also of its transport and thermophysical properties are required.

In terms of the viscosity, the friction theory (*f-theory*)[1] provides a way to link accurate viscosity models to the repulsive and

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attractive pressure terms of an equation of state (EoS). The basic idea of this approach consists in making the analogy between shear flow and two sliding surfaces under shear stress, which is linked to normal stresses through temperature-dependent friction coefficients. In the *f-theory* the normal stresses are given by the repulsive and attractive contributions of the thermodynamic pressure and therefore the shear stress also naturally follows as a balance between repulsive and attractive terms. The *f-theory* has previously been related to the widely used cubic EoS of the van der Waal's type, such as the Soave–Redlich–Kwong (SRK),[2] the Peng–Robinson (PR),[3] or the Patel–Teja (PT).[4] Further, the *f-theory* has been developed into a general model for these EoSs.[5,6] Despite the simplicity of the cubic EoS, it has been shown that the *f-theory* approach can provide, in a simple way, accurate viscosity predictions and modeling results over wide ranges of temperature, pressure, and composition for many fluids of industrial importance and complexity, such as CO_2 + hydrocarbons,[7] light gases,[8] refrigerants,[9] lubricants,[10] refrigerant + lubricant,[11] as well as multicomponent mixtures ranging from natural gas[12,13] to heavy oils[14-16] with viscosities ranging between 10^{-2} and 10^4 mPa·s (or even higher).

However, to overcome the theoretical limitations intrinsic to simple models such as the cubic EoS, molecular-based EoSs have been developed with the aim of achieving a better description of the thermophysical properties that follows from complex molecular physics, such as asymmetry, intricate molecular structure, and association, as well as their interactive collective behavior (mixture properties). One of these molecular-based EoSs is the statistical association fluid theory (SAFT) introduced by Chapman et al.,[17,18] which is based on Wertheim's thermodynamic perturbation theory of first order.[19-22] Along this line, several modifications of the original SAFT EoS have followed, among which is the perturbed-chain statistical association fluid theory (PC-SAFT) by Gross and Sadowski,[23] which has been attracting increasing interest (particularly for applications involving chain molecules).

Thus, in this work, a general *f-theory* model is introduced in conjunction with the PC-SAFT EoS. Similar to other already developed general *f-theory* models, this model is also derived based on the viscosity behavior of the normal alkanes family, from methane to *n*-octadecane. The applicability of this *f-theory* model is further illustrated for mixtures composed of *n*-alkanes and carbon dioxide + *n*-alkanes, which are of relevant industrial interest. Thus, by combining the PC-SAFT EoS with the *f-theory*, in addition to the improved representation of phase behavior and volumetric properties (among other thermophysical properties), an accurate simultaneous representation of the fluid viscosity can also be achieved.

The PC-SAFT Equation of State

In the PC-SAFT EoS,[23] the molecules are assumed to be chains formed by tangentially bonded spheres with the same diameter and dispersive energy. It follows from the perturbation theory that the molecular interactions can be divided into a repulsive and an attractive part of the potential. In this way, the repulsive contribution is defined as a reference fluid without any attractive interactions. The attractive molecular interactions are treated as perturbations to the reference system. Based on this, the PC-SAFT equation, when expressed in terms of the compressibility factor Z, is given as the sum of the ideal gas contribution ($Z_{id} = 1$), a hard-chain contribution (Z_{hc}), and a perturbation contribution of the dispersive forces (Z_{disp}) accounting for the attractive interactions

$$Z = Z_{id} + Z_{hc} + Z_{disp} \tag{1}$$

The PC-SAFT approach is a modification of the SAFT equation by Huang and Radosz.[24,25] The only difference is that in the PC-SAFT EoS the dispersive forces are accounted for by applying a perturbation theory of second order using an expression for the radial pair distribution of a hard-chain reference fluid, whereas in the SAFT equation[24,25] a hard-sphere reference is used in the dispersion term. The exact expressions and definitions for the Z_{hc} and Z_{disp} contributions can be found in Chapman et al.[17,18] and Gross and Sadowski.[23] In general, Z_{hc} is related to three pure component parameters: the segment number m_i, the segment diameter σ_i, and the segment energy parameter ε_i. Also Z_{disp} depends on these three parameters as well as the diameter and energy between unlike segments, σ_{ij} and ε_{ij}, respectively. These two parameters may be obtained by the Berthelot–Lorentz combining rules (see Gross and Sadowski[23]). A binary interaction parameter k_{ij} is introduced in the mixing rule for ε_{ij} to correct the segment–segment interactions of unlike chains.

The Friction Theory

In the friction theory (*f-theory*) for viscosity modeling,[1] the total viscosity η is separated into a dilute gas viscosity term η_0 and a residual friction viscosity term η_f

$$\eta = \eta_0 + \eta_f \tag{2}$$

The dilute gas viscosity is defined as the viscosity given by the kinematics of particles of a finite mass but at the zero density limit, whereas the residual viscosity term is related to friction concepts of classical mechanics. In analogy to the Amontons–Coulomb friction law, in the friction theory the repulsive and attractive contributions to the shear stress are modeled as perturbations away from their corresponding normal stresses.[1] Thus, assuming Newtonian behavior, the friction contribution to the viscosity can be represented according to the following series:

$$\eta_f = \sum_i \kappa_{a,i} p_a^i + \sum_i \kappa_{r,i} p_r^i \tag{3}$$

where p_a and p_r are the attractive and repulsive contributions to the thermodynamic pressure and the $\kappa_{a/r,i}$ are temperature-dependent friction parameters related to friction coefficients between sliding surfaces. In terms of cubic EoS, because of the strong high-pressure dominance of the repulsive term, a linear model for the attractive contribution together with a quadric model for the repulsive has been found to be sufficient to achieve an accurate viscosity representation of a large number of fluids.[1,5] That is, for the previous work related to simple cubic EoS, such as the SRK or PR EoS, it has been shown that the residual friction term can be accurately expressed by a linear function of the attractive pressure p_a and a quadratic function in the repulsive pressure p_r, that is,

$$\eta_f = \kappa_a p_a + \kappa_r p_r + \kappa_{rr} p_r^2 \tag{4}$$

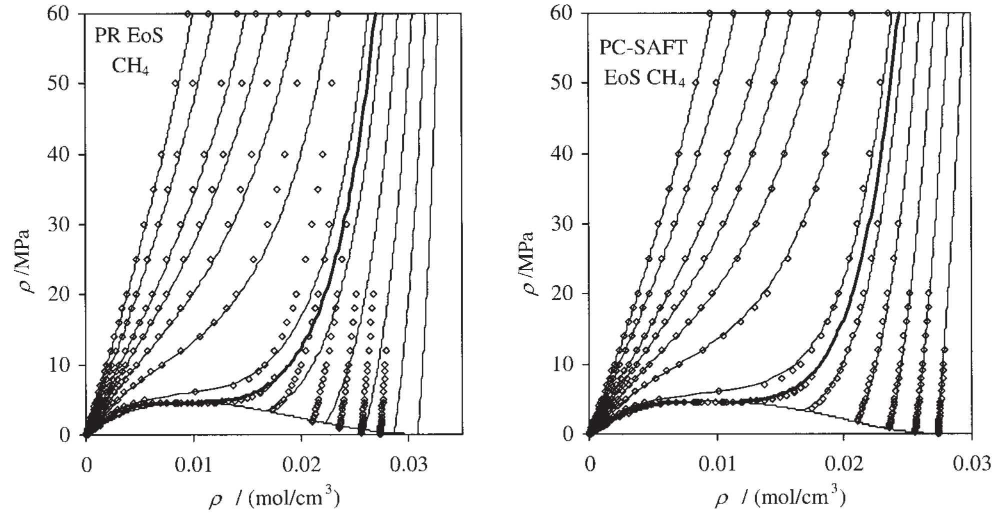

Figure 1. High-pressure *pvT* performance of the PR EoS and the PC-SAFT EoS for methane at the critical isotherm (190.6 K for the PR EoS and 191.4 K as predicted by the PC-SAFT EoS) (—), at 100, 120, 140, 160, 180, 200, 250, 300, 350, 400, 500, and 600 K, and the phase boundary (—); along with the densities by Younglove and Ely[26] (◆).

Also, part of the reason for proposing Eq. 4 as the main model for cubic EoS was numerical efficiency because models of this type are used as core models in highly computational demanding tools such as petroleum reservoir simulators. However, the applications that would be targeted by a model such as the PC-SAFT EoS are of a different type (more focused on the actual physics of the fluids) and the model itself has a substantially higher complexity than that of cubic EoSs. Therefore, for the PC-SAFT EoS a fully quadratic model (for both the repulsive and the attractive pressure terms) of the form

$$\eta_f = \kappa_a p_a + \kappa_{aa} p_a^2 + \kappa_r p_r + \kappa_{rr} p_r^2 \tag{5}$$

is proposed.

Performance of the PC-SAFT EoS at elevated pressure

Before proceeding it is illustrative to underline some of the basic motivations for extending the *f-theory* to the PC-SAFT EoS. One of the problems encountered with the application of cubic EoS–based *f-theory* models to complex fluids, such as heavy or degraded reservoir fluids, is the compressibility response of such simple models under high pressure.[16] This problem may be related to the mathematical and theoretical limitations of the van der Waals repulsive term as it is extended to high-pressure conditions. This issue not only pertains to complex molecules but is also important even for simple molecules, such as methane. Indeed, one major problem that cubic EoSs have is their poor high-pressure performance, even for light fluids of industrial relevance such as natural gas. This problem is clearly illustrated in Figure 1 where a comparison of the methane *pvT* methane performance between the PR EoS and the PC-SAFT EoS is depicted along with the recommended methane data by Younglove and Ely.[26] It is clear that for high-pressure applications involving large amounts of methane (such as natural gas) the PR EoS, and for that matter all cubic EoSs, will not perform in a satisfactory manner. Indeed, no volume translation or any other artificial scheme can correct the pathological compressibility behavior illustrated by the PR EoS isotherms in Figure 1, given that their problem lies in their intrinsic failure to accurately represent the pressure dependency with the volume, especially its derivatives. On the other hand, the performance of the PC-SAFT model, as illustrated in Figure 1, is clearly superior—one possible reason that the PC-SAFT EoS delivers such an improved high-pressure compressibility performance may be linked to the step potential used in its derivation (see Gross and Sadowski[23]).

In terms of viscosity, the PC-SAFT EoS also shows some advantages, although not as obvious as in the case of their *pvT* performance. To explore this issue let us consider a linear *f-theory* model for both the PR EoS and the PC-SAFT EoS, that is,

$$\eta_f = \kappa_a p_a + \kappa_r p_r \tag{6}$$

In the case of the PC-SAFT EoS, the dispersive term is identified as the attractive pressure p_a term, that is,

$$p_a = p_{disp} \tag{7}$$

whereas the repulsive pressure term p_r is defined as

$$p_r = p_{id} + p_{hc} \tag{8}$$

Regarding the temperature dependency of the friction constants, consistent with previous work,[1] a simple exponential dependency of the following form is suggested:

$$\kappa_a = a_1 \exp[\Gamma - 1] + a_2 \exp[2\Gamma - 2] \tag{9}$$

and

$$\kappa_r = b_1 \exp[\Gamma - 1] + b_2 \exp[2\Gamma - 2] \tag{10}$$

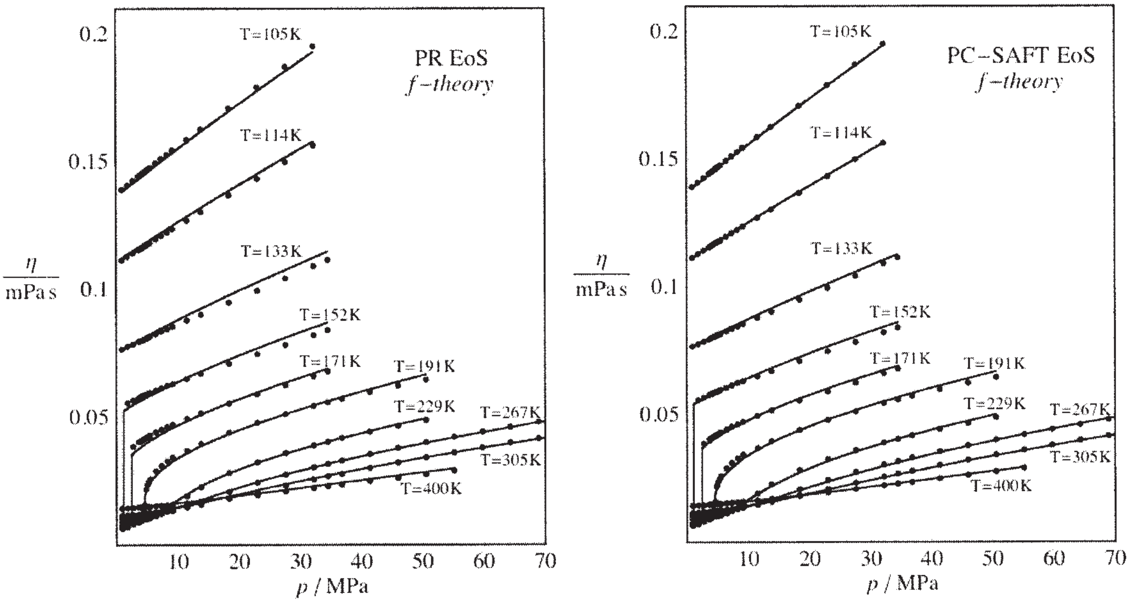

Figure 2. Linear PR and PC-SAFT *f-theory* viscosity models for methane, along with the recommended data by Zéberg-Mikkelsen[27] (●).

Thus, the corresponding linear *f-theory* models consist of four adjustable parameters for each substance (a_1, a_2, b_1, and b_2).

Figure 2 shows a comparison of the viscosity results for the methane correlations using the PR EoS and the PC-SAFT EoS. As it appears from this figure the linear model seems to give good results for both EoSs, although the PC-SAFT EoS delivers a better performance in the region of transition between a light fluid and a dense one (reduced temperature between 0.8 and 1.2). On the other hand, Figure 3 shows similar results but now for a correlation corresponding to a much heavier molecule: *n*-pentadecane. In the case of the *n*-pentadecane correlations it is clear that, if the range of application is to be extended up to 100 MPa, both linear models fail to perform satisfactorily. Thus, similar to previous works,[1,5,6] for high-pressure applications a quadratic model will still be required for an *f-theory* model based on the PC-SAFT EoS. Finally, it is remarked that, because a highly accurate general PC-SAFT *f-theory* viscosity model will be presented next, the specific correlation parameters corresponding to the linear models shown in Figures 2 and 3 are irrelevant because such correlations were made for illustration purposes only.

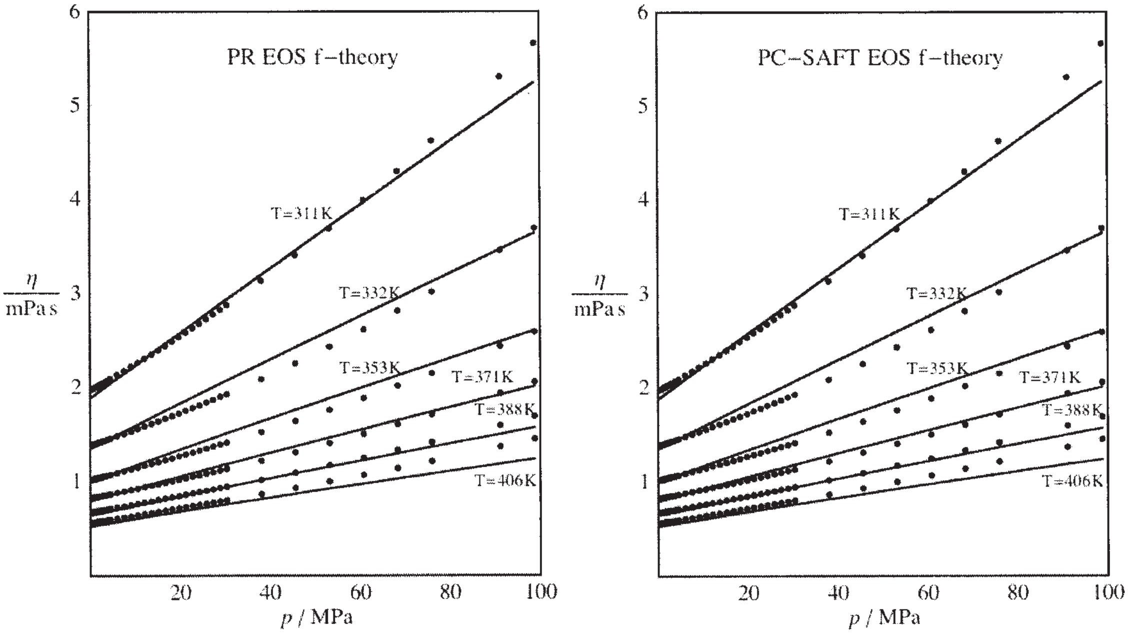

Figure 3. Linear PR and PC-SAFT *f-theory* viscosity models for *n*-pentadecane, along with the recommended data by Zéberg-Mikkelsen[27] (●).

The general viscosity model

Based on the general concepts of the *f-theory*, a general quadratic viscosity model has been derived and coupled to the PC-SAFT EoS. Given the already intrinsic complexity of the PC-SAFT model and for the sake of accuracy, we propose a residual friction contribution model that is quadratic on both the repulsive and the attractive terms and is dependent on two scaling parameters, η_a and η_r:

$$\eta_f = \eta_a\left[\tilde{\kappa}_a\left(\frac{p_a}{p_c}\right) + \tilde{\kappa}_{aa}\left(\frac{p_a}{p_c}\right)^2\right] + \eta_r\left[\tilde{\kappa}_r\left(\frac{p_r}{p_c}\right) + \tilde{\kappa}_{rr}\left(\frac{p_r}{p_c}\right)^2\right] \tag{11}$$

For the model proposed in Eq. 11 the reduced friction coefficients $\tilde{\kappa}_a$, $\tilde{\kappa}_{aa}$, $\tilde{\kappa}_r$, and $\tilde{\kappa}_{rr}$ have been found to correlate with the temperature T and the segment number m in an accurate manner for the normal alkanes family. It should also be pointed out that, for proper functional reduction, p_c must always be the critical pressure that follows from satisfying the critical conditions with the PC-SAFT EoS for a given pure component (not a tabulated p_c).

For the temperature- and segment number–dependent reduced friction coefficients the following empirical expressions have been found appropriate to describe the viscosity up to 100 MPa of pure *n*-alkanes ranging from methane to *n*-octadecane:

$$\begin{aligned}\tilde{\kappa}_a = {} & a_{0,0} + a_{1,0}(\exp[\Gamma - 1] - 1) + a_{2,0}(\exp[2\Gamma - 2] - 1) + a_{3,0}(\exp[3\Gamma - 3] - 1) + \frac{a_{0,1}}{m} + \frac{a_{0,2}}{m^2} \\ & + \frac{a_{1,1}(\exp[\Gamma - 1] - 1) + a_{2,1}(\exp[2\Gamma - 2] - 1) + a_{3,1}(\exp[3\Gamma - 3] - 1)}{m} \\ & + \frac{a_{1,2}(\exp[\Gamma - 1] - 1) + a_{2,2}(\exp[2\Gamma - 2] - 1) + a_{3,2}(\exp[3\Gamma - 3] - 1)}{m^2}\end{aligned} \tag{12}$$

$$\begin{aligned}\tilde{\kappa}_r = {} & b_{0,0} + b_{1,0}(\exp[\Gamma - 1] - 1) + b_{2,0}(\exp[2\Gamma - 2] - 1) + b_{3,0}(\exp[3\Gamma - 3] - 1) + \frac{b_{0,1}}{m} + \frac{b_{0,2}}{m^2} \\ & + \frac{b_{1,1}(\exp[\Gamma - 1] - 1) + b_{2,1}(\exp[2\Gamma - 2] - 1) + b_{3,1}(\exp[3\Gamma - 3] - 1)}{m} \\ & + \frac{b_{1,2}(\exp[\Gamma - 1] - 1) + b_{2,2}(\exp[2\Gamma - 2] - 1) + b_{3,2}(\exp[3\Gamma - 3] - 1)}{m^2}\end{aligned} \tag{13}$$

$$\begin{aligned}\tilde{\kappa}_{aa} = {} & A_{0,0} + \frac{A_{0,1}}{m} + \frac{A_{0,2}}{m^2} \\ & + \frac{A_{2,1}(\exp[2\Gamma - 2] - 1) + A_{3,1}(\exp[3\Gamma - 3] - 1)}{m} \\ & + \frac{A_{2,2}(\exp[2\Gamma - 2] - 1) + A_{3,2}(\exp[3\Gamma - 3] - 1)}{m^2}\end{aligned} \tag{14}$$

$$\begin{aligned}\tilde{\kappa}_{rr} = {} & B_{0,0} + \frac{B_{0,1}}{m} + \frac{B_{0,2}}{m^2} \\ & + \frac{B_{2,1}(\exp[2\Gamma - 2] - 1) + B_{3,1}(\exp[3\Gamma - 3] - 1)}{m} \\ & + \frac{B_{2,2}(\exp[2\Gamma - 2] - 1) + B_{3,2}(\exp[3\Gamma - 3] - 1)}{m^2}\end{aligned} \tag{15}$$

with

$$\Gamma = \frac{T_c}{T} \tag{16}$$

and where T_c must also be the critical temperature that satisfies the critical conditions with the PC-SAFT EoS (not a tabulated T_c).

Clearly, the actual friction coefficients in Eq. 5 will follow from the reduced ones according to the following expressions:

$$\kappa_a = \eta_a \frac{\tilde{\kappa}_a}{p_c} \tag{17}$$

$$\kappa_r = \eta_r \frac{\tilde{\kappa}_r}{p_c} \tag{18}$$

$$\kappa_{aa} = \eta_a \frac{\tilde{\kappa}_{aa}}{p_c^2} \tag{19}$$

and

$$\kappa_{rr} = \eta_r \frac{\tilde{\kappa}_{rr}}{p_c^2} \tag{20}$$

The universal friction constants ($a_{i,j}$, $A_{i,j}$, $b_{i,j}$, and $B_{i,j}$) in Eqs. 12–15 have been estimated using a database containing smoothed experimental viscosities of normal alkanes from

Table 1. Scaling Parameters $\eta_{,a}$ and $\eta_{,r}$ for the General PC-SAFT *f-Theory* Viscosity Model

Compound	$\eta_{,a}$ (μP)*	$\eta_{,r}$ (μP)
Methane	8.15957	48.7410
Ethane	9.04189	49.9325
Propane	1.29954	65.0437
n-Butane	−6.24267	75.2528
n-Pentane	−6.42895	75.1365
n-Hexane	−17.0600	86.3043
n-Heptane	−32.7790	98.8131
n-Octane	−49.7901	112.585
n-Decane	−78.6746	133.007
n-Dodecane	−94.6198	140.528
n-Tridecane	−84.6536	142.394
n-Tetradecane	−98.6187	142.742
n-Pentadecane	−102.101	147.090
n-Hexadecane	−93.7225	145.777
n-Octadecane	−104.067	150.037
Carbon dioxide	−16.1322	119.251
Nitrogen	2.28277	57.7935

*1 μP = 10^{-4} mPa · s.

Table 2. Friction Constants for the General PC-SAFT *f-Theory* Viscosity Model

Attractive Friction Constants		Repulsive Friction Constants	
$a_{0,0}$	0.144998	$b_{0,0}$	0.333075
$a_{1,0}$	−0.0305382	$b_{1,0}$	0.302822
$a_{2,0}$	0.223166	$b_{2,0}$	−0.145200
$a_{3,0}$	−0.00686973	$b_{3,0}$	−0.0149881
$a_{0,1}$	−2.37354	$b_{0,1}$	−0.154596
$a_{0,2}$	1.55529	$b_{0,2}$	−0.0122148
$a_{1,1}$	0.555650	$b_{1,1}$	−0.0391957
$a_{2,1}$	−1.31634	$b_{2,1}$	0.435213
$a_{3,1}$	0.331436	$b_{3,1}$	−0.0866662
$a_{1,2}$	−1.93953	$b_{1,2}$	0.175047
$a_{2,2}$	1.02853	$b_{2,2}$	−0.655495
$a_{3,2}$	0.132005	$b_{2.0}$	0.247205
$A_{0,0}$	0.00157800	$B_{0,0}$	−0.000574904
$A_{0,1}$	−0.00142498	$B_{0,1}$	0.000374863
$A_{0,2}$	−0.0222979	$B_{0,2}$	0.00262223
$A_{2,1}$	0.00681810	$B_{2,1}$	0.000466001
$A_{3,1}$	−0.000466511	$B_{3,1}$	0.00182595
$A_{2,2}$	−0.0258567	$B_{2,2}$	0.00494766
$A_{3,2}$	0.0110935	$B_{3,2}$	−0.00374101

methane to *n*-octadecane over wide ranges of temperature and pressure.[27] This database was also used to derive the previously published general *f-theory* models for the SRK, PR, and PT EoSs.[5,6] Essentially, the model parameterization follows the same ideas as for the previous general models, that is, a perturbation away from the critical isotherm. However, a major difference with cubic EoSs follows from the fact that in the case of the PC-SAFT EoS (as well as all more advanced EoSs) the model does not deliver a universal critical compressibility (Z_c), which is reflected in the mathematical form of Eqs. 12–15. Additionally, for the sake of accuracy and model flexibility two scaling parameters (η_a and η_r), rather than one, have been introduced. The regression of the general PC-SAFT *f-theory* model parameters has been carried out iteratively with alternate optimizations of the scaling parameters in Eq. 11 and the universal constants in Eqs. 12–15 until a quadratic residual defined by relative viscosities was minimized. The obtained scaling parameters are given in Table 1, whereas the universal friction constants in Eqs. 12–15 are given in Table 2.

In Table 3, the corresponding average absolute deviation (AAD) and maximum absolute deviation (MxD) obtained by the model are reported along with the temperature range and the maximum applicable pressure. The deviations reported in Table 3 for the general PC-SAFT *f-theory* are excellent and satisfactory for most engineering applications. The maximum deviations are reasonably low values that are found in regions that correspond to extreme conditions of high experimental uncertainty, that is, around the critical point, at a light gas phase, or for a phase at low-temperature and high-pressure conditions.

In Figure 4 a very good agreement between the predicted viscosities of propane and the recommended values of Vogel et al.[28] is shown. In the case of the 600 K isotherm a higher deviation is observed, which may be explained by the fact that such an isotherm is outside the tuning range of all models, given that no experimental information is available up to that temperature. Actually, any application of the general PC-SAFT *f-theory* model outside the ranges reported in Table 3 ought to be considered as extrapolations. However, in Figure 5 the deviation between the predicted viscosities of *n*-decane by the general PC-SAFT *f-theory* model and experimental literature values[29-36] in the range 278–478 K is shown up to 150 MPa. This figure reveals that a satisfactory extrapolation to pressures higher than the reported range (0–100 MPa) in Table 3 is achieved.

Further, the general PC-SAFT *f-theory* model has been applied to the viscosity modeling of carbon dioxide[37] and nitrogen.[38] The estimated scaling parameters for these two compounds are reported in Table 1, whereas the modeling results are given in Table 3.

For pure alkanes higher than *n*-hexane (m = 3.0576) a simple correlation between the viscosity scaling parameters η_a and η_r and the segment number m can be obtained with the following asymptotic expressions:

$$\eta_a = -124.491 + 5.88015/m + 1023.46/m^2 \tag{21}$$

and

Table 3. Modeling Deviation Results for the PC-SAFT *f-Theory* Viscosity Model

Compound	T/T_c Range	Max P/P_c	AAD%	MxD%
Methane	0.55–2.50	20.0	1.08	4.52
Ethane	0.35–1.60	11.3	0.76	4.83
Propane	0.30–1.29	13.0	1.18	4.75
n-Butane	0.35–1.04	18.0	1.21	9.14
n-Pentane	0.64–1.16	30.0	1.32	9.08
n-Hexane	0.56–1.08	35.0	1.52	16.5
n-Heptane	0.50–1.00	35.0	0.97	8.07
n-Octane	0.45–1.00	40.0	1.02	7.74
n-Decane	0.45–0.76	48.0	0.70	2.50
n-Dodecane	0.45–0.60	55.0	0.97	5.40
n-Tridecane	0.44–0.53	60.0	1.24	2.96
n-Tetradecane	0.42–0.54	60.0	1.38	4.49
n-Pentadecane	0.44–0.58	65.0	0.88	4.91
n-Hexadecane	0.41–0.52	70.0	1.11	7.15
n-Octadecane	0.42–0.55	80.0	1.39	7.94
Carbon dioxide	0.66–1.97	13.5	4.35	15.0
Nitrogen	0.63–4.75	29.4	3.20	14.9

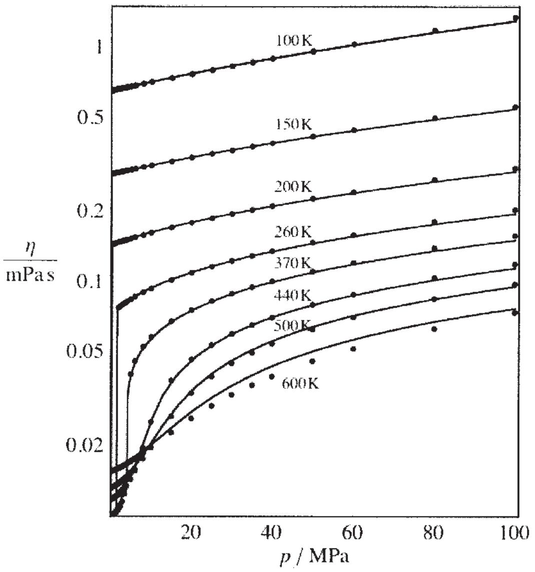

Figure 4. Viscosity η of propane at various isotherms vs. pressure *p* predicted by the general PC-SAFT *f-theory* model (—), along with the recommended values of Vogel et al.[28] (●).

$$\eta_r = 160.376 + 44.6249/m - 852.173/m^2 \tag{22}$$

The required dilute gas viscosity term has been calculated by the dilute gas viscosity model of Chung et al.,[39] which can represent the dilute gas viscosity of a wide range of fluids (including those studied in this work) within an uncertainty of 1.5%. In this dilute gas viscosity model the tabulated values for the critical molar volume and the critical temperature are required along with the acentric factor and the molecular weight. In this work the required tabulated parameters have been taken from Poling et al.[40] However, it should be pointed out that as the compound becomes heavier (above *n*-decane) the dilute gas limit contribution becomes less important and it may even be neglected, given that such fluids will likely be of relevance only for condensed phases.

Application to Mixtures

In the case of an *n*-component mixture the total viscosity can be expressed with basically the same type of mixing rules as in previous works.[1,5,6] That is, in the case of the dilute gas viscosity, the mixture contribution may be approximated using the following mixing rule:

$$\eta_0 = \exp\left(\sum_{i=1}^{n} x_i \ln \eta_{0,i}\right) \tag{23}$$

and, consistent with previous works, the mixture mixing rules for the friction coefficients are given by

$$\kappa_a = \sum_{i=1}^{n} z_i \kappa_{a,i} = \sum_{i=1}^{n} z_i \eta_{a,i} \frac{\tilde{\kappa}_{a,i}}{p_{c,i}} \tag{24}$$

$$\kappa_{aa} = \sum_{i=1}^{n} z_i \kappa_{aa,i} = \sum_{i=1}^{n} z_i \eta_{a,i} \frac{\tilde{\kappa}_{aa,i}}{p_{c,i}^2} \tag{25}$$

$$\kappa_r = \sum_{i=1}^{n} z_i \kappa_{r,i} = \sum_{i=1}^{n} z_i \eta_{r,i} \frac{\tilde{\kappa}_{r,i}}{p_{c,i}} \tag{26}$$

$$\kappa_{rr} = \sum_{i=1}^{n} z_i \kappa_{rr,i} = \sum_{i=1}^{n} z_i \eta_{r,i} \frac{\tilde{\kappa}_{rr,i}}{p_{c,i}^2} \tag{27}$$

where in all cases the subindex *i* denotes the corresponding pure component property. However, in the case of the PC-SAFT EoS a modified estimation of the mass-weighted fraction z_i appeared to give improved results. Thus, in this work, the mass weighted z_i fraction is estimated using the relation

$$z_i = \frac{x_i m_i \varepsilon_i}{MW_i F_w} \tag{28}$$

with

$$F_w = \sum_{i=1}^{n} x_i \frac{m_i \varepsilon_i}{MW_i} \tag{29}$$

where *x* is the mole fraction, MW is the molar mass, *m* is the segment number, and ε is the segment energy parameters in the PC-SAFT EoS. Thus, for mixture calculations Eqs. 24–27 are substituted in Eq. 5 and the p_a and p_r are taken directly from the PC-SAFT EoS according to Eqs. 7 and 8 and using the EoS mixing rules suggested by Gross and Sadowski.[23]

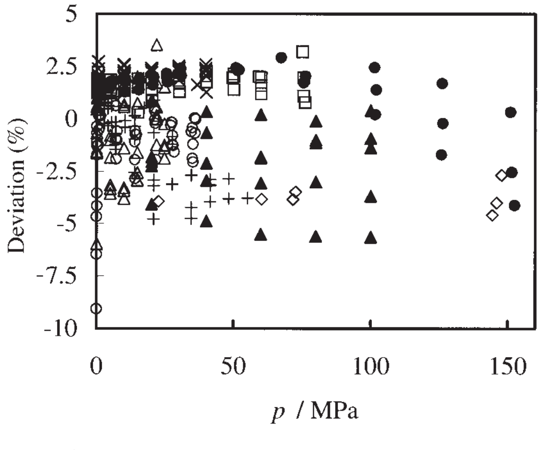

Figure 5. Comparison of viscosities for *n*-decane vs. pressure p shown as the deviation (η_c/η_e − 1) × 100 between the calculated values by the general PC-SAFT *f-theory* model (η_c) and the experimental values (η_e).

(+) Lee and Ellington[29]; (○) Carmichael et al.[30]; (×) Knapstad et al.[31,32]; (●) Oliveira and Wakeham[33]; (△) Estrada-Baltazar et al.[34]; (◇) Tohidi et al.[35]; (□) Audonnet and Padua [36]; (▲) Ducoulombier et al.[50]

Table 4. Predictive Results for the General PC-SAFT *f-Theory* Model Applied to *n*-Alkane Mixtures

System	NM*	NP**	*T* (K)	*P* (MPa)	AAD%	MxD%
$C_1 + C_2$[41]	3	250	120–300	1.5–35	3.35	19.9
$C_1 + C_3$[42]	4	282	311–411	0.1–55	2.36	6.57
$C_1 + n\text{-}C_4$[43]	1	104	278–478	0.1–36	4.50	7.95
$C_1 + n\text{-}C_6$[44]	3	53	293–451	15–43	4.93	12.1
$C_1 + n\text{-}C_{10}$[32,36]	7	200	292–431	9.8–76	6.84	21.9
$n\text{-}C_5 + n\text{-}C_8$[45]	9	295	298–373	0.1–25	3.98	12.4
$n\text{-}C_5 + n\text{-}C_{10}$[46]	9	312	298–373	0.1–25	3.17	14.3
$n\text{-}C_6 + n\text{-}C_7$[47]	2	53	303–323	0.1–72	1.19	3.68
$n\text{-}C_7 + n\text{-}C_8$[48]	4	172	292–480	0.1–49	2.68	9.22
$n\text{-}C_7 + n\text{-}C_9$[47]	2	57	303–323	0.1–72	1.11	3.19
$n\text{-}C_7 + n\text{-}C_{11}$[49]	2	57	303–323	0.1–72	3.29	7.21
$n\text{-}C_8 + n\text{-}C_{10}$[34]	9	324	298–373	0.1–25	2.97	6.37
$n\text{-}C_{10} + n\text{-}C_{16}$[50]	3	54	313–353	0.1–100	3.44	9.33
$n\text{-}C_5 + n\text{-}C_8 + n\text{-}C_{10}$[51]	15	530	298–373	0.1–25	3.41	15.7
$n\text{-}C_{10} + n\text{-}C_{12} + n\text{-}C_{14} + n\text{-}C_{16}$[50]	1	18	313–353	0.1–100	1.25	4.62

*Number of mixtures.
**Number of points.

n-Alkane mixture results

A thorough evaluation of the PC-SAFT friction theory mixing rules has been performed on several binary through quaternary mixtures. The resulting AAD and MxD values are reported in Table 4 along with the number of points (NP), number of mixtures (NM), and the temperature and pressure ranges. In general, it can be appreciated from Table 4 that the accuracy of the mixture predictions is within or close to the experimental uncertainty. The larger deviation found for the methane + *n*-decane system may arise from factors such as the experimental uncertainty itself or the large acentric difference between methane and *n*-decane. In fact, this system also provided the largest deviations in the PR and SRK *f-theory* models,[1,5] which in the last cases are slightly higher than for the PC-SAFT *f-theory* model. Figures 6 and 7 show the viscosity prediction for the binary system methane + propane and the quaternary system *n*-decane + *n*-dodecane + *n*-tetradecane + *n*-hexadecane, respectively. A comparison of the general PC-SAFT *f-theory* model with the other general *f-theory* models for the PR, SRK, or PT EoS[5,6] shows that similar results are obtained for the studied *n*-alkane mixtures, although a more accurate EoS is used in this work. This supports the prodigious effort that has been given to tuning the scaling parameters of the cubic EoS. However, it is to be expected that as chain molecules become larger an EoS such as the PC-SAFT should deliver a more robust overall performance (including phase and density behavior) than that of a cubic EoS.

In this work, the required binary interaction parameters k_{ij} in the PC-SAFT EoS were taken from Gross and Sadowski.[23] For mixtures where no k_{ij} parameters are reported in Gross and Sadowski, it was found appropriate to use $k_{ij} = 0.01$, except for methane + ethane and methane + *n*-decane. For the system methane + ethane, the k_{ij} was determined by fitting PC-SAFT to experimental isothermal vapor–liquid equilibria (VLE) measurements[52-57] in the range 150–280 K. The temperature dependency of the k_{ij} is shown in Figure 8, revealing that the k_{ij} values appear to follow a linear behavior as a function of the temperature:

$$k_{ij} = -0.033594 + 0.00015494T \tag{30}$$

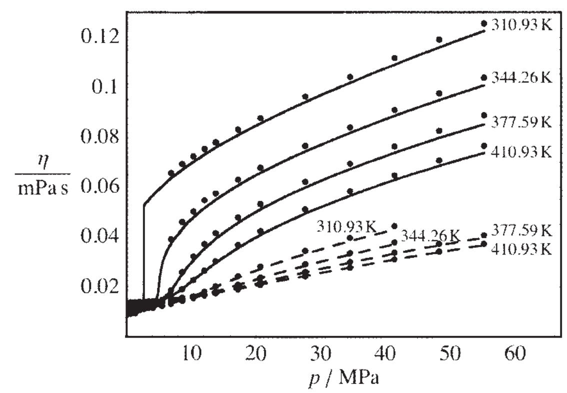

Figure 6. Viscosity η of the binary methane + propane mixture at various isotherms vs. pressure p predicted by the general PC-SAFT *f-theory* model for 22.07 mol % methane (—) and for 79.1 mol % methane (– – –), along with the experimental values of Giddings et al.[42] (●).

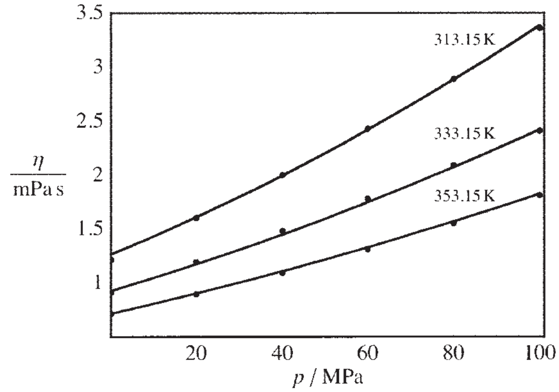

Figure 7. Viscosity η of the quaternary mixture 31.44 mol % *n*-decane + 26.26 mol % *n*-dodecane + 22.55 mol % *n*-tetradecane + 19.75 mol % *n*-hexadecane at various isotherms vs. pressure p predicted by the general PC-SAFT *f-theory* model (—), along with the experimental values of Ducoulombier et al.[50] (●).

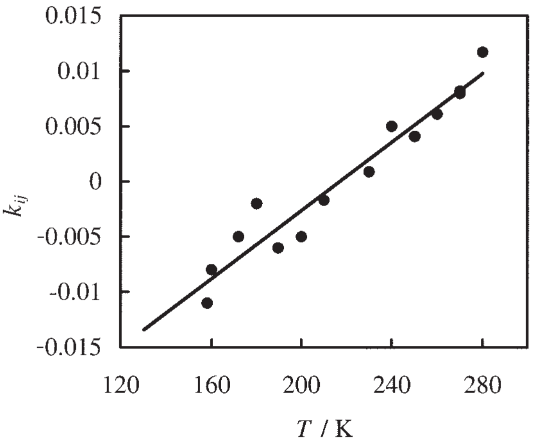

Figure 8. Temperature dependency of adjusted PC-SAFT k_{ij} binary interaction parameters for methane + ethane (●).

where T is given in K.

An adjustment of the k_{ij} for methane + *n*-decane has also been performed to better reproduce the VLE behavior of this system within the temperature range of the considered viscosity data. The reason is that the k_{ij} value of 0.056 reported in Gross and Sadowski[23] was correlated against VLE data in the range 423 to 583 K, which is outside the temperature range of the considered viscosity data. The temperature dependency of the estimated K_{ij} values obtained by fitting the PC-SAFT EoS to experimental VLE data [58-63] is shown in Figure 9, revealing a linear dependency as a function of the temperature, which can be expressed as

$$k_{ij} = -0.035905 + 0.00019412T \tag{31}$$

with T given in K.

Carbon dioxide + n-alkane mixtures

In addition to the viscosity prediction of *n*-alkane mixtures and to illustrate the capability of the general PC-SAFT *f-theory* model to more dissimilar mixtures, the viscosities of mixtures composed of carbon dioxide + *n*-alkanes have been predicted. The obtained AAD and MxD values are reported in Table 5 along with NP, NM, and the temperature and pressure range. In general it can be appreciated from Table 5 that the obtained results are satisfactory and close to the uncertainty reported for the experimental viscosities.

For carbon dioxide mixtures the required binary interaction parameters k_{ij} in the PC-SAFT EoS were taken from Gross and Sadkowski,[23] except for carbon dioxide + ethane, where the reported $k_{ij} = 0.09$ in García et al.[69] was used. For mixtures, where no k_{ij} parameters are given in Gross and Sadkowski,[23] the reported uniform value $k_{ij} = 0.12$ as suggested in García et al.[69] was used. For this type of mixtures the results obtained with the general PC-SAFT *f-theory* are better than those obtained by the general PT, PR, and SRK *f-theory* models.[5,6] In the case of the general PC-SAFT *f-theory* model an overall AAD% of 4.58 is obtained compared with the 6.48, 5.67, and 6.83% obtained with the PT, PR, and SRK EoS general *f-theory* models, respectively.

Conclusion

A general *f-theory* viscosity model coupled to the PC-SAFT EoS has been developed. This *f-theory* model has been shown to provide satisfactory results for the modeling of the viscosity of the normal alkanes family, carbon dioxide, and nitrogen. In addition, an evaluation of the performance of the general *f-theory* model has been performed for several *n*-alkane and carbon dioxide + *n*-alkane mixtures over wide ranges of temperature and pressure, showing a good prediction of the viscosity within uncertainties satisfactory for most industrial and research applications. This accurate viscosity prediction is achieved using simple mixing rules for the friction coefficients. Further, the general PC-SAFT *f-theory* model can potentially be extended to the viscosity modeling and prediction of crude oils based on the mass characterization procedure already introduced in an *f-theory*–related work[16]—the subject of a forthcoming report. In addition, the general PC-SAFT *f-theory* approach will also be applied to other asymmetric mixtures such as refrigerant + lubricant systems.

In addition, despite the fact that the more accurate PC-SAFT EoS has been applied, it should be noted that the performance of the general PC-SAFT *f-theory* model for the considered mixtures in this work is practically similar to the performance of the general *f-theory* models based on the SRK, PR, and PT EoSs.[5,6] The reason is certainly related to the fact that the *f-theory* is built on a balance between attractive and repulsive contributions, which makes it a more robust approach compared to models that directly depend on density—although the model indirectly does depend on density. However, the combination of the *f-theory* with a more theoretically sound EoS, such as the SAFT models, does provide extended advantages regarding other phase and thermophysical properties as well as a more theoretically sound description of the fluid physics. For example, it would be of theoretical and industrial relevance to have an accurate representation of transport properties linked to other thermophysical properties or complex phenomena such as the barotropic behavior (recently discussed also using the PC-SAFT model as the reference EoS[70]) or to models capable of delivering an accurate representation of high-order derivatives because many important thermophysical properties do depend of such derivatives.[71]

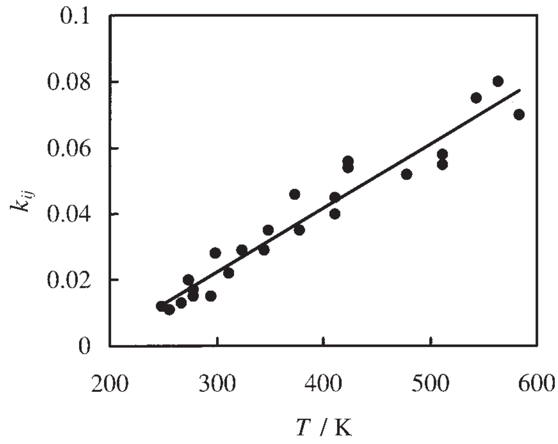

Figure 9. Temperature dependency of adjusted PC-SAFT k_{ij} binary interaction parameters for methane + *n*-decane (●).

Table 5. Predictive Results for the General PC-SAFT *f-Theory* Model Applied to Carbon Dioxide + *n*-Alkane Mixtures

System	NM*	NP**	T (K)	P (MPa)	AAD%	MxD%
$CO_2 + C_1$[64]	3	132	323–474	3.4–70	2.95	8.76
$CO_2 + C_2$[65,66]	6	362	210–500	2.1–61	5.60	22.2
$CO_2 + n\text{-}C_{10}$[67,68]	6	69	311–403	6.7–35	2.60	12.7
$CO_2 + n\text{-}C_5 + n\text{-}C_{10}$[68]	2	10	354–401	2.5–4.9	1.50	3.26
$CO_2 + n\text{-}C_4 + n\text{-}C_6 + n\text{-}C_{10}$[68]	2	10	324–395	2.5–4.9	7.61	17.9
$CO_2 + n\text{-}C_5 + n\text{-}C_6 + n\text{-}C_7 + n\text{-}C_{10}$[68]	2	8	360–395	2.5–4.9	2.80	6.04

*Number of mixtures.
**Number of points.

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Notation

k_{ij} = binary interaction parameter
MW = molecular weight
m = molecular segment number
p = pressure
p_a = attractive pressure
p_c = critical pressure
p_{disp} = dispersive pressure
p_{id} = ideal pressure ($P = RT/v$)
p_{hc} = hard-core pressure
p_r = repulsive pressure
R = universal gas constant
T = temperature
T_c = critical temperature
v = molar volume
v_c = critical molar volume
x = mole fraction
Z = compressibility factor
z = volume-weighted fraction

Greek letters

ε = molecular segment energy parameter
η = viscosity
η_0 = dilute gas viscosity
η_f = residual friction term
$\eta_{,a}$ = attractive viscosity scaling parameter
$\eta_{,r}$ = repulsive viscosity scaling parameter
Γ = reciprocal reduced temperature defined in Eq. 16
κ_a = linear attractive friction coefficient
κ_r = linear repulsive friction coefficient
κ_{aa} = quadratic attractive friction coefficient
κ_{rr} = quadratic repulsive friction coefficient
σ = molecular segment diameter
ω = acentric factor

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