Generalized SAFT-DFT/DMT Model for the Thermodynamic, Interfacial, and Transport Properties of Associating Fluids: Application for \textit{n}-Alkanols

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We have developed a “global” crossover (GC) statistical associating fluid theory (SAFT) equation of state (EOS) for associating fluids that incorporates nonanalytic scaling laws in the critical region and in the limit of low densities, \( \rho \to 0 \), is transformed into the ideal-gas equation EOS. Unlike the crossover SAFT EOS developed earlier, the new GC SAFT EOS contains a so-called kernel term and reproduces the asymptotic scaling behavior of the isochoric heat capacity in the one- and two-phase regions. In addition, we develop on the basis of the density functional theory (DFT) a GC SAFT-DFT model for the surface tension. In the second step, using the GC SAFT EOS and the decoupled-mode theory (DMT), we have developed a generalized GC SAFT-DMT model for transport coefficients that reproduces the singular behavior of the thermal conductivity of pure fluids in the critical region. Unlike the DMT model based on the asymptotic crossover EOS, the GC SAFT-DMT model is valid in the entire fluid state region at \( T \geq T_b \) (where \( T_b \) is the binodal temperature), and at \( \rho \to 0 \) reproduces the dilute gas contributions for the transport coefficients. A comparison was made with experimental data for methanol, ethanol, and higher \textit{n}-alkanols. For \textit{n}-alkanols, the GC SAFT-DFT/DMT model contains the same number of the adjustable parameters as the original classical SAFT EOS but reproduces with high accuracy the PVT, VLE, isochoric, and isobaric specific heats, surface tension, and thermal conductivity data close to and far from the critical point.

1. Introduction

In associating fluids such as \textit{n}-alkanols, strong attractive interactions between molecules result in the formation of molecular clusters that have considerable effect on the thermodynamic and structural properties of the species. Due to their high polarity and strong self-association, \textit{n}-alkanols, and in particular methanol, are complex fluids that are extremely challenging for both experimental and theoretical study. Experiments dealing with the thermodynamic and transport properties over a wide temperature range of such a thermally labile species as associating fluids are often hindered by chemical reactions, including decomposition. Therefore, extrapolation of different empirical and semi-empirical multi-parameter equations of state (EOS) for \textit{n}-alkanols in the range of conditions where no experimental data were used for their optimization is often unreliable and in general is not recommended. On the other hand, molecular-based equations of state, such as statistical associating fluid theory (SAFT), employ equations that have been developed as an alternative to empirical EOS for associating liquids. In its original\(^{1-3}\) and modified\(^{4-8}\) form, SAFT cannot reproduce the critical parameters \( T_c, P_c, \) and \( \rho_c \) simultaneously and is therefore incapable of reproducing different thermodynamic properties such as vapor–liquid equilibria (VLE), PVT, densities, specific heats, enthalpies, and excess properties in the gas and liquid phases simultaneously with the same set of the system-dependent parameters. In addition, all of these analytical EOS fail to reproduce the nonanalytical, singular behavior of fluids in the critical region, caused by long-scale fluctuations in density.

A general procedure for incorporating long-range density fluctuations into any classical—analytical equation was proposed by Kiselev\(^9\) based on renormalization-group theory This procedure has been successfully applied to the SAFT,\(^10-12\) SAFT-BACK,\(^13\) and SAFT-VR\(^14,15\) EOS. In all cases, this method produces a thermodynamically self-consistent and accurate crossover EOS near to and far from the critical points of pure fluids. Recently, in combination with the generalized crossover density functional (DFT) and decoupled mode theory (DMT), this procedure has been also extended to the interfacial\(^14,16\) and transport\(^17\) properties of pure fluids.

In this paper, we continue a study initiated in our previous works for cubic\(^16,17\) and SAFT EOS.\(^11\) First, we have developed a “global” crossover (GC) SAFT EOS for methanol, ethanol, and higher \textit{n}-alkanols, which unlike the crossover SAFT EOS developed earlier\(^11\) contains a so-called kernel term\(^18\) and reproduces the asymptotic scaling behavior of the isochoric heat capacity in the critical region. Second, on the basis of the GC SAFT equation and the density functional theory, we developed a generalized GC SAFT-DFT model for surface tension. Combining the GC SAFT equation with the

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crossover decoupled mode theory, we have also developed a GC SAFT-DMT model for the transport properties and have compared this model with experimental thermal conductivity and thermal diffusivity data for methanol and ethanol.

We proceed as follows. In section 2, we describe a general procedure for transforming the analytical SAFT equation into the crossover form and obtain a GC SAFT EOS in closed analytical form. In section 3, we develop a GC SAFT EOS for n-alkanols and provide an extensive comparison with experimental data. In section 4, we present a GC SAFT-DFT model for the surface tension. A generalized crossover SAFT-DMT model for the transport properties is considered in section 5. Our results are summarized and discussed in section 6.

2. Thermodynamic Model

2.1. Classical SAFT Equation. In this work, for a reference classical SAFT EOS we adopt the model developed by Huang and Radosz.4,5 The molar residual Helmholtz energy (Ares) in this model consists of three terms:

$$\frac{A_{\text{res}}}{RT} = a_{\text{res}} = a_{\text{seg}} + a_{\text{chain}} + a_{\text{assoc}}$$  \hspace{1cm} (1)

where \(a_{\text{seg}}\) is the Helmholtz energy due to segment–segment interactions, \(a_{\text{chain}}\) is the incremental Helmholtz energy due to chain formation, and \(a_{\text{assoc}}\) is the incremental Helmholtz energy due to association.

The segment contribution is given by4,5

$$\begin{equation}
a_{\text{seg}} = m(a_0^{\text{hs}} + a_0^{\text{disp}}) \hspace{1cm} (2)
\end{equation}$$

where \(m\) is the number of segments per molecule and \(a_0^{\text{hs}}\) is the Helmholtz energy of hard-sphere fluids per segment given by Carnahan and Starling:19

$$\begin{equation}a_0^{\text{hs}} = 4\eta - 3\eta^2 \hspace{1cm} (3)
\end{equation}$$

where \(\eta = \pi/6N_Amp^3\) is the reduced density, and

$$\begin{equation}d = \frac{1 - C \exp\left(-3\frac{a_0^{\text{hs}}}{k_BT}\right)}{C} \hspace{1cm} (4)
\end{equation}$$

is the temperature-dependent segment diameter. In eqs 1–4, \(R\) is the gas constant; \(N_A\) is Avogadro’s number; \(\rho\) is the molar density; \(\sigma\) is the center-to-center distance between two segments, at which the pair potential of the real fluid is zero (the temperature-independent segment diameter); \(k_B\) is the Boltzmann constant; \(C = 0.12\) for all fluids in this work; and \(u^0\) is the temperature-independent well depth of the square-well potential. The temperature-independent segment diameter (\(\sigma\)) is related to the temperature-independent segment molar volume in a close-packed arrangement defined per mole of segments:

$$\begin{equation}u^0 = \frac{\pi N_A \sigma^3}{6} \hspace{1cm} (5)
\end{equation}$$

where \(\tau = \sqrt{2}\pi/6\). The dispersion part in eq 2 (\(a_0^{\text{disp}}\)) is given by the Chen–Kreglewski expression:20

$$\begin{equation}a_0^{\text{disp}} = \sum_i \sum_j D_{ij} \left(\frac{u}{k_BT}\right)^\frac{1}{T} \hspace{1cm} (6)
\end{equation}$$

where the coefficients \(D_{ij}\) are universal constants; \(u\) is the temperature-dependent well depth defined as

$$\begin{equation}u = u^0\left(1 + \frac{\epsilon}{k_BT}\right) \hspace{1cm} (7)
\end{equation}$$

and the parameter \(\epsilon/k_B\), which in general is related to the critical temperature and Pitzer’s acentric factor \(\omega\), for SAFT molecules was set4 to \(\epsilon/k_B = 10\).

The chain contribution (\(a_{\text{chain}}\)) in eq 1 is given by

$$\begin{equation}a_{\text{chain}} = -(m - 1) \ln g_{hs}^{\text{ch}}(d) \hspace{1cm} (8)
\end{equation}$$

where \(g_{hs}(d) = (2 - \eta)/(2(1 - \eta)^2\) is the radial distribution function of the hard-sphere fluid at contact.

The association contribution (\(a_{\text{assoc}}\)) in eq 1 is given by

$$\begin{equation}a_{\text{assoc}} = \sum_{A=1}^n \left(\ln X_A - rac{X_A^2}{2}\right) + \frac{n(\Gamma)}{2} \hspace{1cm} (9)
\end{equation}$$

where \(n(\Gamma)\) is the number of association sites on the molecule and \(X_A\) is the fraction of molecules that are not bonded at site A. The expression for \(X_A\) is written in the form

$$\begin{equation}X_A = (1 + N_A\rho \sum_{B=1}^n X_B ^{\Delta A B})^{-1} \hspace{1cm} (10)
\end{equation}$$

where \(\Delta A B\) is the association strength given by

$$\begin{equation}\Delta A B = \sigma^3 \chi^{AB} \left[\exp\left(\frac{\epsilon^{AB}}{k_BT}\right) - 1\right] g_{hs}^{\text{ch}}(d) \hspace{1cm} (11)
\end{equation}$$

where \(\epsilon^{AB}\) is the well depth of the site–site potential and \(\sigma^3 \chi^{AB}\) is a measure of the volume available for bonding. To obtain specific expressions for \(a_{\text{assoc}}\) and \(X_A\), one has to hypothesize the number of association sites and make simplifying approximations for the association strength of site–site interactions. Here, similar to our previous work,11 n-alkanols are modeled as associating chain molecules with two association sites (i.e., model 2B).

The total number of SAFT parameters for associating fluids is five; namely, the segment number (\(m\)), the segment volume (\(u^0\) or \(\sigma\)), the well depth of the segment–segment potential (\(u^0\)), site–site (\(\epsilon^{AB}\)) interaction, and the volume bonding parameter (\(\sigma^3 \chi^{AB}\)). The classical critical molar density and temperature (i.e., \(\rho_{oc}\) and \(T_{oc}\)) are obtained by solving the criticality conditions:

$$\begin{equation}\left(\frac{\partial P}{\partial \rho}\right)_{T_{oc}} = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_{oc}} = 0 \hspace{1cm} (12)
\end{equation}$$

where \(P\) is the pressure. Once \(\rho_{oc}\) and \(T_{oc}\) are known, the critical pressure \(P_{oc}\) can be also obtained.

2.2. Crossover SAFT Equation. To obtain a GC EOS, which in the critical region reproduces all known scaling laws and in the limit of low densities is reduced to the ideal-gas EOS, we follow the crossover approach developed by Kiselev.9 Following this approach, we first
represent the dimensionless Helmholtz free energy \( a(T, v) = A(T, v) / RT \) in the form

\[
a(T, v) = \Delta a(\Delta T, \Delta v) + a_{\text{bg}}(T, v)
\]

where the critical part of the dimensionless Helmholtz free energy

\[
\Delta a(\Delta T, \Delta v) = a^\text{res}(\Delta T, \Delta v) - a^\text{res}(\Delta T) + \bar{P}_0(\Delta T)\Delta v - \ln(\Delta v + 1)
\]

and the background contribution is given by

\[
a_{\text{bg}}(T, v) = a^\text{res}(T) + a^\text{id}(T) - \bar{P}_0(T)\Delta v
\]

where the critical part of the dimensionless Helmholtz free energy is given by

\[
\Delta a(\Delta T, \Delta v) = a^\text{res}(\Delta T, \Delta v) - a^\text{res}(\Delta T) + \bar{P}_0(\Delta T)\Delta v - \ln(\Delta v + 1)
\]

and the background contribution is given by

\[
a_{\text{bg}}(T, v) = a^\text{res}(T) + a^\text{id}(T) - \bar{P}_0(T)\Delta v
\]

In eqs 14 and 15, \( v = 1 / \rho \) is a molar volume, \( \Delta T = T / T_0 - 1 \) and \( \Delta v = u / v_0 - 1 \) are dimensionless distances from the classical critical temperature \( T_0 \) and molar volume \( v_0 \), respectively; \( \bar{P}_0(T) = P_0(T, v_0) \) is the dimensionless pressure; \( a^\text{res}(T) = a^\text{res}(T, v_0) \) is the dimensionless residual part of the Helmholtz energy along the critical isochore \( v = v_0 \); and \( a^\text{id}(T) \) is the dimensionless temperature-dependent ideal-gas Helmholtz free energy.

In the second step, we replace the classical values of \( \Delta T \) and \( \Delta v \) in the critical part \( \Delta a(\Delta T, \Delta v) \) with the renormalized values:

\[
\bar{r} = \frac{r}{T^*}
\]

\[
\bar{\varphi} = \frac{\varphi}{T^*}
\]

where \( \alpha = 0.11, \beta = 0.325, \gamma = 2 - 2\beta - \alpha = 1.24, \) and \( \Delta_1 = 0.51 \) are universal nonclassical critical exponents; \( r = T / T_c - 1 \) is a dimensionless deviation of the temperature from the true critical temperature \( T_c \); \( \varphi = v / v_c - 1 \) is a dimensionless deviation of the molar volume from the true critical molar volume \( V_c \); \( T_c = (T_c - T_{\text{oc}}) / T_{\text{oc}} \approx 1 \) and \( \Delta v_c = (v_c - v_{\text{oc}}) / v_{\text{oc}} \approx 1 \) are dimensionless shifts of the critical temperature and volume, respectively; and \( Y(r, \varphi) \) denotes a crossover function.

In this work, for the crossover function \( Y(r, \varphi) \), we use a simple phenomenological expression obtained by Kiselev and co-workers:

\[
Y(q) = \frac{\left[ \frac{q}{1 + q} \right]^{2\Lambda_1}}{1 + q}
\]

where following our recent work for the generalized cubic EOS, \( q = \frac{\varphi}{1 + \varphi} \) we find the renormalized distance to the critical point \( q \) from a solution of the crossover sine model (SM):

\[
\left( q^2 - \frac{r}{G_1} \right)^{\frac{1}{4}} \left[ 1 - \frac{p^2}{4b^2 q^2 G_1} \left( 1 - \frac{r}{q^2 G_1} \right) \right] = \frac{b_2}{m_0 G_1} \left[ \frac{1}{1 + v_1 \exp(-10\varphi)} + d_1 \right] - \frac{d_1}{2} \frac{m_0 G_1}{r}
\]

where the coefficients \( m_0, v_1, d_1, \) and the Ginzburg number \( G_1 \) are the system-dependent parameters, while the universal parameters \( p^2 \) and \( b^2 \) can be set equal to the linear model (LM) parameter \( p^2 = b^2 = b_{1M}^2 = 1.359 \). The crossover SM as given by eq 19 is physically equivalent to the crossover sine model developed earlier, but with a different empirical term.
\[ v_1 = -2.15 \times 10^{-3} + 3.98 \times 10^{-4} Gi^{-1}, \]
\[ d_1 = 4.443 - 0.143 Gi^{-1} \quad (25) \]

where the Ginzburg number in \( n \)-alkanols was found to be a simple linear function of the molar mass \( M_w \):

\[ Gi^{-1} = 3.40 + 0.227 M_w \quad (26) \]

In accordance with eq 23, we represent the parameter \( a_{20} \) in the kernel term in the form

\[ a_{20} = \frac{2A^+}{Gi^a} (2 - \alpha)(1 - \alpha) \quad (27) \]

where the asymptotic critical amplitude \( A^+ \) was set equal to the corresponding amplitude in the parametric crossover model\(^{20}\)

\[ A^+ = Z_c \frac{ak\gamma(1 - 1)}{2ab_{LM}} \quad (28) \]

where the parameters \( a \) and \( k \) in eq 28 have been determined from the corresponding-state relations developed earlier by Kiselev et al.\(^{26}\)

\[ a = 15.645(1 + 19.220 \Delta \omega), \]
\[ k = 1.15(1 + 0.3327 \Delta \omega^{0.885}) \quad (29) \]

where \( \Delta \omega = \omega - 0.011 \) is the difference between the acentric factor of the fluid of interest and the acentric factor of a reference system (methane in ref 26). In general, the second parameter in the kernel term \( (a_{21}) \) can be considered as an adjustable parameter in the GC SAFT EOS. However, according to the more rigorous renormalization-group theory calculations performed by Belyakov and Kiselev,\(^{27}\) the ratio \( a_{21}/a_{20} \) in eq 23 is a system-independent constant. Therefore, in this work we set \( a_{21} = -0.3a_{20} \), which appears to be a good approximation for the parameter \( a_{21} \) in \( n \)-alkanols. After this redefinition, only five adjustable parameters remain. If the actual critical temperature \( (T_c) \) and density \( (\rho_c) \) of the fluid of interest are known, the critical shifts \( (\Delta T_c \) and \( \Delta \rho) \) and the critical compressibility \( (Z_c = P_d/R_0 T_c) \) are known as well, and the GC SAFT EOS for associating fluids contains the same number of adjustable parameters as the original SAFT EOS (i.e., \( m, v^0, u^0, e^{AB}, \) and \( k^{AB} \)). Otherwise, \( T_c \) and \( \rho_c \) should be considered as additional adjustable parameters of the model.

The first system that we consider here is methanol. Because of the high polarity and strong association between molecules, methanol is challenging to model; therefore, it is an interesting test for the GC SAFT EOS. The parameters \( m, v^0, u^0, e^{AB}, \) and \( k^{AB} \) for methanol have been found from a fit of the GC SAFT EOS to experimental one-phase region \( PVT \) data obtained by Zubarev et al.,\(^{28}\) Finkelstein and Stiel,\(^{29}\) Straty et al.,\(^{30}\) and Bazaev et al.,\(^{31}\) the liquid density data obtained by Machado and Street,\(^{32}\) and the VLE data obtained by Ramsay and Young,\(^{33}\) Donham,\(^{34}\) Ambrose and Sprake,\(^{35}\) and Abdulagatov et al.\(^{36}\) Although the thermodynamic properties of methanol have been studied extensively by different researchers and by different experimental methods, as was shown by Abdulagatov et al.,\(^{37}\) there is still a large variation in the published values of the critical temperature and density for methanol. Therefore, in this work, the critical parameters for methanol have been found from a fit of the GC SAFT EOS to new experimental \( C_V \) data asymptotically close to the critical point obtained recently by Abdulagatov et al.\(^{37}\) These values are very close to the critical temperature \( T_c = 512.78 \) K and density \( \rho_c = 267.8 \) kg \( \cdot \) m\(^{-3} \) obtained by Bazaev et al.\(^{31}\) from analysis of their \( PVT \) data for methanol. The critical pressure \( P_c = 8.196 \) MPa calculated with GC SAFT EOS (eq 24) is also close to the value obtained by Bazaev et al.,\(^{31}\) \( P_c = 8.10 \) MPa, indicating thermodynamic self-consistency of the GC SAFT EOS applied to methanol.

The predictions of the GC SAFT model for methanol as compared with experimental data are shown in Figures 1–6. As one can see, there is very good agreement between the GCS model and the experimental data. The GC SAFT EOS reproduces the saturated pressure data at temperatures between 200 K and \( T_c \) with an average absolute deviation (AAD) of 0.64% \( (n = 49) \), the liquid density with AAD of 0.53% \( (n = 39) \), and the vapor density with AAD of 3.5% \( (n = 39) \). In the one-phase region at densities less than 2\( \rho_c \), the GC SAFT EOS reproduces the \( PVT \) data with an AAD of 1.7% \( (n = 262) \) and the liquid densities at densities greater than or equal to 2\( \rho_c \) with an AAD of 1.2% \( (n = 261) \). We would especially like to emphasize the excellent agreement between the predictions of the GC SAFT EOS and experimental one-phase \( C_p \) and one- and two-phase \( C_V \) data in the critical region shown in Figures 4–6. The dashed curves in Figures 4 and 5 correspond to the values calculated with the IUPAC EOS.\(^{38}\) As one can see, the GC SAFT and IUPAC EOS\(^{38}\) give very close predictions for the isobaric heat capacity along the near critical isobar at \( P = 10 \) MPa. However, unlike the GC SAFT EOS, the multi-parameter EOS developed by de Reuck and Craven\(^{39}\) does not even qualitatively reproduce an asymptotic behavior of the isochoric heat capacity in the critical region.

In the second step, we developed the GC SAFT EOS for ethanol and higher \( n \)-alkanols up to heptan-1-ol. For ethanol, we adopt the same critical density as employed earlier by Kiselev and Ely\(^{16}\) in the generalized corresponding states model, while for the critical temperature...
we use a value obtained by Polikhronidi et al.\textsuperscript{39} from an analysis of their new experimental CV data in the critical region of ethanol. All other system-dependent parameters in the GC SAFT EOS for ethanol have been found from a fit of the GC SAFT EOS to VLE data\textsuperscript{35,40,41} and one-phase PVT data obtained by Golubev et al.\textsuperscript{42} and by Lo and Stiel.\textsuperscript{43} For all other n-alkanols, we adopt values of the critical parameters employed earlier by Kiselev and Ely.\textsuperscript{16} The classical SAFT parameters have been found from a fit of the GC SAFT EOS to the VLE and one-phase PVT data taken from refs 35, 44, and 45 for propan-ol-1; refs 35 and 45–48 for butan-1-ol; refs 49–53 for pentan-1-ol; refs 49, 50, and 53–55 for hexan-1-ol; and refs 56–58 for heptan-1-ol. The values of all system-dependent parameters of the GC SAFT EOS for n-alkanols are listed in Table 1. Experimental saturated
pressure and liquid and vapor density data in comparison with values calculated with the crossover GC SAFT EOS are shown in Figure 7. For all fluids shown in Figure 7, the GC SAFT EOS reproduces the saturated pressure and liquid density data with an AAD of less than 1% and the vapor densities with an AAD of about 3–4%. Figures 8 and 9 compare the predictions of the GC SAFT EOS with experimental one-phase PVT (Figure 8) and one- and two-phase C\textsubscript{v} (Figure 9) data for ethanol. Again, excellent agreement between the predictions of the GC SAFT EOS and experimental data for both PVT and C\textsubscript{v} data sets is observed. The dashed lines in Figure 9 correspond to the values of the isochoric heat capacity calculated with a new fundamental equation for ethanol developed by Dillon and Penoncello.\textsuperscript{59} As one can see, this EOS, similar to the IUPAC EOS for methanol considered above (see Figure 5), fails to reproduce the C\textsubscript{v} data in the critical region, while the GC SAFT EOS even asymptotically close to the critical point, at \( T \rightarrow \pm T_{c} \), is in excellent agreement with experimental data.

4. Surface Tension

As we mentioned above, GC SAFT EOS based on the sine model can be extended into the metastable region;
free energy density in the two-phase region at \( \rho v \leq \rho \leq \rho_L \); and \( \mu(T, \rho_L) = (\partial F/\partial \rho_T) \) is the chemical potential of the bulk fluid along the saturation curve \( \rho = \rho_L(T) \). In eq 31, the Helmholtz free energy \( F(T, \rho) = a(T, \nu)RT \) is calculated with the GC expression for \( a(T, \nu) \) (eq 20) and the parameter \( c_0 \), which is directly related to the asymptotic critical amplitude of the correlation length:\(^{60}\)

\[
\xi_0 = (c_0 \Gamma_0^+)^{1/2}
\]  

(eq 32)

\( \Gamma_0^+ \) is an amplitude in the asymptotic power law \( \chi_T(\rho_c, \tau) = \Gamma_0^+ \tau^{-\gamma} \) for the reduced isothermal compressibility \( \chi_T = \rho T (\partial^2 \rho/\partial T^2) \rho_T^{-2} T^{-1} \) can be estimated for associating fluids with the expression\(^{16}\)

\[
c_0 = (1 - \kappa_0)^{1/2} k_B T \rho_c^{1/3}
\]  

(eq 33)

where the system-dependent coefficient \( \kappa_0 < 1 \) can be extracted from the surface tension measured at \( T = 0.7T_c \), or nearby values.

In this work, we applied the GC SAFT-DFT model for the calculation of the surface tension in methanol, ethanol, and butan-1-ol. Comparisons of the predicted values of the surface tension with experimental data are shown in Figures 10 and 11. As one can see from Figure 10, in a wide temperature range, at \( 0.5 T < T < T_c \), a better result for the surface tension in methanol can be achieved with the parameter \( \kappa_0 = 0.23 \) (or \( \xi_0 = 0.104 \) nm). However, in the asymptotic critical region at \( |\tau| \leq 0.02 \), the GC SAFT-DFT model reproduces the surface tension data better with the parameter \( \kappa_0 = 0.16 \) or \( \xi_0 = 0.114 \) nm. For ethanol and butan-1-ol, good agreement with experimental data is achieved with the parameter \( \kappa_0 = 0.16 \), or the same with the critical amplitudes \( \xi_0 = 0.111 \) nm for ethanol and \( \xi_0 = 0.124 \) nm butan-1-ol, respectively (see Figure 11).

5. Thermal Conductivity

For the thermal conductivity of the \( n \)-alkanols, we use a crossover decoupled-mode theory (DMT) model for the transport coefficients of pure fluids and fluid mixtures developed by Kiselev and Kulikov.\(^{61,62}\) In the limit of pure components, the crossover expression for the thermal conductivity takes the form\(^{61–63}\)

\[
\lambda = \frac{k_B T \rho_c C_P}{6 \pi \eta b} \Omega(z) + \lambda_b
\]  

(eq 34)

where \( \eta b \) is the viscosity, and \( \lambda_b \) is a background part of the thermal conductivity that can be represented as a sum of the dilute-gas and the residual contributions

\[
\lambda_b(\rho, T) = \lambda^o(T) + \Delta \lambda(\rho, T)
\]  

(eq 35)

where \( \lambda^o \) is the dilute-gas thermal conductivity, which depends only on temperature, and \( \Delta \lambda \) is the residual thermal conductivity. The crossover function \( \Omega(z) = \Omega(q_D \xi) \) in eq 34 is given by

\[
\Omega(z) = \frac{2}{\pi} \tan^{-1}(z) - \frac{1}{\sqrt{1 + y_{1D} z^2}} \tan^{-1}\left(\frac{z}{\sqrt{1 + y_{1D} z^2}}\right)
\]  

(eq 36)

where

\[
y_{1D} = \frac{6 \pi \eta b^2}{k_B T \rho q_D (\phi_1 + \phi_{1D})}, \quad y_1 = \frac{k_B T \rho_c C_P}{6 \pi \eta b \xi_0} \xi_0
\]  

(eq 37)

In eqs 34–37, \( q_D \) is a cutoff wavenumber, the renormalized correlation length is given by\(^{63}\)

\[
\xi = \xi_{1D} \exp\left(-\frac{1}{q_D \xi_{1D}}\right)
\]  

(eq 38)

where \( \xi_{1D} = \xi_0 \sqrt{\chi_0 T_0} \) corresponds to the Ornstein–Zernike approximation for the correlation length\(^{60}\), and \( \phi_{1D} = \phi(k_{1D} \xi) = \phi(z) \) is the dynamical scaling function\(^{61,62}\)

\[
\phi(z) = \frac{3(1 + z^2 + (z^3 - z^{-1}) \tan^{-1}(z))}{4 z^2 (1 + z^2)}
\]  

(eq 39)

calculated at a constant value of the wavenumber \( k_{1D} = 0.1 q_D \). Asymptotically close to the critical point at \( q_D \xi_{1D} \gg 1 \), the parameter \( y_1 \gg 1 \), the crossover function \( \Omega(z) \) approaches unity, and the thermal conductivity along
the critical isochore diverges at \( r \to +0 \) as \( \lambda \propto r^{-\gamma/2} \). Far from the critical point, at \( q_{D} \ll 1 \), the crossover function \( \Omega(z) \to 0 \), and the thermal conductivity \( \lambda \) becomes equal to its background part \( \lambda_{0} \).

In this work, we applied the GC SAFT-DMT model for the calculation of the thermal conductivity of methanol and ethanol in a wide range of temperatures and pressures, including the critical and supercritical regions. All thermodynamic properties in the GC SAFT-DMT model (eqs 36–39) are calculated with the GC SAFT EOS, with the cutoff wavenumber \( q_{\mathrm{D}}^{-1} = 3\zeta_{0} \), where for the critical amplitude \( \zeta_{0} \) we adopt the values obtained in the GC SAFT-DFT model for the surface tension

\[
\zeta_{0}^{\text{CH}_3} = 0.114 \text{ nm}, \quad \zeta_{0}^{\text{OH}} = 0.111 \text{ nm}, \quad \zeta_{0}^{\text{CH}_2} = 0.124 \text{ nm} \quad (40)
\]

The shear viscosity \( (\eta_{s}) \) in eqs 34 and 37 is an analytic function of the temperature and density. For methanol, we adopted the expression given by Xiang et al.\(^{64}\) that represents the data in the liquid and vapor phase up to pressures of about 500 MPa to about 3\%. For the viscosity of ethanol, we are not aware of any wide-ranging, accurate correlations, so we present one here. In this work, \( \eta_{s} \) has been represented as the sum of a dilute-gas contribution and a residual term\(^{65}\)

\[
\eta_{s}(\rho, T) = \eta^{0}(T)[1 + B_{\eta}(T)\rho] + \Delta\eta(\rho, T) \quad (41)
\]

The term \( \eta^{0}(T) \) represents the viscosity in the limit of zero density, \( B_{\eta}(T) \) is the second virial coefficient for viscosity based on the Rainwater–Friend theory,\(^{66,68}\) and \( \Delta\eta(\rho, T) \) is the contribution that represents the higher-density terms as a function of the absolute temperature \( T \) and density \( \rho \).

We approximated the viscosity \( \eta^{0} \) of ethanol in the zero-density limit using a polynomial in temperature\(^{67}\)

\[
\eta^{0}(T) = -1.03116 + 3.48379 \times 10^{-2} T - 6.50264 \times 10^{-6} T^{2} \quad (42)
\]

where \( T \) is in K and the viscosity is in \( \mu \text{Pa\cdot}s \). The Rainwater–Friend term\(^{66,68}\) is found using

\[
B_{\eta}(T) = \frac{N_{A}\alpha^{3}B_{\eta}^{*}(T^{\text{w}})}{\sigma^{3}} \quad (43)
\]

where \( N_{A} \) is the Avogadro constant, and we used the correlation for \( B_{\eta}^{*} \) given by Vogel et al.\(^{65}\)

\[
B_{\eta}^{*}(T^{\text{w}}) = \sum_{i=0}^{s} b_{i}(T^{\text{w}})^{i} \quad (44)
\]

with parameters \( b_{i} \) and the exponents \( t_{i} \) taken from Vogel et al.\(^{65}\) that are given in Table 2. For the Lennard–Jones parameters we adopted the values \( \sigma = 0.453 \text{ nm} \) and \( \epsilon/k = 362.6 \text{ K} \) given in Reid et al.\(^{69}\)

\[
\begin{array}{cccccc}
\text{Table 2. Parameters for the Second Viscosity Virial Coefficient,}^{65} \text{ Equation 44} \\
\hline
i & b_{i} & t_{i} & i & b_{i} & t_{i} \\
0 & 19.572 881 & 5 & 0 & 2491.659 7 & 6.25 \\
1 & 218.739 99 & -0.25 & 2 & 787.260 88 & -1.50 \\
2 & 1015.322 6 & -0.50 & 7 & 14.085 45 & -2.50 \\
3 & 2471.012 5 & -0.75 & 8 & -0.346 641 58 & -5.50 \\
4 & 3473.782 5 & -0.75 & 6 & -0.346 641 58 & -5.50 \\
\end{array}
\]

Table 3. Parameters for the Viscosity Correlation, Equations 45 and 46

\[
\begin{array}{cccc}
\text{coefficient} & \text{coefficient} \\
\hline
a_{20} & 0.131194057 & a_{32} & -0.110578307 \\
a_{21} & -0.382246084 & c_{1} & 23.7222956 \\
c_{2} & -0.38264465 & c_{2} & -3.83204465 \\
c_{3} & -0.0805700894 & c_{1} & 12.7568864 \\
c_{31} & 0.153811778 \\
\end{array}
\]

We expressed the higher density terms \( \Delta\eta(\rho, T) \) in terms of the reduced density \( \rho = \rho_{\text{B}} \) and the reduced temperature \( T = T/\theta_{k} \) using the form\(^{70}\)

\[
\Delta\eta(\rho, T) = 1000 \left( \frac{3}{2} \sum_{j=2}^{\infty} c_{j} T^{j} \right) \quad (45)
\]

\[
\delta_{0} = c_{2} + c_{3} \sqrt{T} \quad (46)
\]

where the viscosity is in \( \mu \text{Pa\cdot}s \) and the reducing parameters were \( T_{\theta} = 513.9 \text{ K} \) and \( \rho_{\text{B}} = 5.991 \text{ mol/L} \).

We used primarily the data of Golubev and Petrov\(^{71}\) as given in Golubev\(^{72}\) and several additional, smaller data sets\(^{73}–^{78}\) that cover a wide range of temperature and pressure conditions that included pressures up to 100 MPa and temperatures from 273 to 538 K, and regressed the data with the statistical package ODRPACK\(^{79}\) in order to obtain the coefficients given in Table 3. The densities of ethanol used in the regression were obtained from the equation of state of Dillon and Penoncello.\(^{80}\) The correlation represents the Golubev and Petrov\(^{71,72}\) data set with an average absolute deviation of 1.86\%, the Assael and Polimatidou\(^{73}\) data to 0.7\%, Papaoannou and Panayiotou\(^{74}\) data to 2.1\%, Papanastasiou and Ziogas\(^{75}\) data to 0.4\%, Lee et al.\(^{76}\) data to 1.0\%, Bingham et al.\(^{77}\) data to 1.6\%, and Phillips and Murphy\(^{78}\) data to 1.1\%.

We approximated the dilute-gas contribution for the thermal conductivity of methanol by adopting the correlation\(^{80}\)

\[
\lambda^{(0)}(T) = 5.7992 \times 10^{-7} T^{1.7862} \quad (47)
\]

while for ethanol we used the equation recommended by the DIPPR DIADEM program\(^{80}\)

\[
\lambda^{(0)}(T) = \frac{-10.109 \times 10^{-3} T^{0.6475}}{1.0 - 7332/T - 268000/T^{2}} \quad (48)
\]

where the temperature unit is K and the thermal conductivity units are W-m\(^{-1}\)-K\(^{-1}\). For the residual contribution in both fluids, methanol and ethanol, we use here a polynomial in temperature and density

\[
\Delta\lambda_{i}(\rho, T) = \sum_{i=1}^{3} b_{i1} + b_{i2} T \left( \frac{\rho}{\rho_{\text{B}}} \right)^{i} \quad (49)
\]

which has recently been shown to accurately represent hydrocarbon fluids such as isobutane\(^{81}\) butane\(^{82}\) and propane.\(^{83}\) The parameters \( b_{i1} \) (\( i = 1–3, j = 1, 2 \)) in the residual contribution have been found from a fit of the GC SAFT-DMT model to the selected data sets for methanol\(^{84}–^{90}\) and ethanol\(^{84,91,92}\) that cover a wide range of temperature and pressure conditions above and below the critical point. The values of the coefficients \( b_{i1} \) in eq 49 for methanol and ethanol are listed in Table 4, and comparisons with the experimental thermal
conductivity data are shown in Figures 12–14. For both substances, very good agreement between the GC SAFT-DMT model and experimental thermal conductivity data is observed. The GC SAFT-DMT model reproduces all thermal conductivity data for methanol \((n = 430)\) and ethanol \((n = 230)\) with an AAD of 0.85%. The sharp maxima of the thermal conductivity observed at \(P = 10\) MPa and \(T = 512\) K in methanol (see Figure 12) and at near critical pressures at \(T = 520\) K for ethanol (see Figure 14) correspond to the critical enhancements caused by long-range density fluctuations as described by the first term in right-hand side of eq 34. In Figure 15 we show the thermal conductivity for methanol as a function of density calculated along the selected isobars and isotherms with the GC SAFT-DMT model. As one can see, the maxima of the thermal conductivity, observed at \(\rho = \rho_c\), increase drastically as the pressure and temperature approach their critical values.

The thermal diffusivity \((D_T = \lambda/\rho CP)\) is another property that exhibits a strong anomalous behavior in the critical region. Since the thermal diffusivity requires a simultaneous calculation of the thermal conductivity, isobaric heat capacity, and density, it is a good test for the physical self-consistency of the model. In Figure 16 we show comparisons between GC SAFT-DMT predictions and thermal diffusivity data in methanol obtained by Bushirov. Agreement between the GC SAFT-DMT calculations and experimental data is fairly good. Since no experimental \(D_T\) data have been used for the optimization of the GC SAFT-DMT model, we consider this result as additional evidence of the physical self-consistency of the GC SAFT DMT model.

### 6. Conclusions

The molecularly based SAFT EOS has proven to be very versatile for the prediction of phase equilibria in associating fluids. However, in common with all analytic EOS, the SAFT EOS exhibits classical behavior in the critical region rather than the nonanalytical, singular behavior caused by the density fluctuations, which

<table>
<thead>
<tr>
<th>parameter</th>
<th>methanol</th>
<th>ethanol</th>
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</thead>
<tbody>
<tr>
<td>(b_{1,1})</td>
<td>3.11820803E−01</td>
<td>1.06917458E−01</td>
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<td>(b_{2,1})</td>
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<tr>
<td>(b_{2,2})</td>
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<td>6.14073818E−02</td>
</tr>
<tr>
<td>(b_{3,2})</td>
<td>−3.20792858E−02</td>
<td>−1.00317135E−02</td>
</tr>
</tbody>
</table>

- **Figure 12.** Thermal conductivity data for methanol\(^{28,84}\) (symbols) with predictions of the GC SAFT-DMT model (curves).
- **Figure 13.** Thermal conductivity data for ethanol along isobars\(^{91}\) (empty symbols) and along the saturated curve\(^{94}\) (filled symbols) as a function of temperature with predictions of the GC SAFT-DMT model (curves).
- **Figure 14.** Thermal conductivity data for ethanol along isobars (left) and along isotherms (right) as a function of density with predictions of the GC SAFT-DMT model (curves).
- **Figure 15.** Thermal conductivity data for methanol\(^{28,84}\) (symbols) along isobars (left) and along isotherms (right) as a function of pressure with predictions of the GC SAFT-DMT model (curves).
Figure 16. Thermal diffusivity data for methanol along the isobars\(^9\) (symbols) as a function of temperature with predictions of the GC SAFT-DMT model (curves).

anomalously increase in the vicinity of the critical point of pure fluids. As a result, accurate agreement over the whole phase diagram cannot be obtained with analytic SAFT equations and they must be localized to either the critical or subcritical regions. The first step in developing a crossover SAFT equation, which incorporates the scaling laws in the critical region and is transformed into the original analytical rates, is developing a crossover SAFT equation for the critical or subcritical regions. The first step in SAFT equations and they must be localized to either the critical or subcritical regions. As a result, accurate agreement over the whole fluid phase diagram representing not only the VLE, but also the \(PVT\) properties in long-chain, polar, and associating fluids. However, except for the CR SAFT EOS for propan-1-ol,\(^18\) no attempt was made to develop a GC SAFT EOS for the VLE, \(PVT\), \(C_P\), and \(C_V\) properties, and until now no generalized crossover SAFT model for the thermodynamic, interfacial, and transport properties in associating fluids has been developed.

In this work, we have developed a GC SAFT EOS model for \(n\)-alkanols by incorporating the crossover approach developed by Kiselev into the analytical SAFT equation for associating fluids developed by Huang and Radosz.\(^4\) With only four adjustable parameters, the GC SAFT EOS describes the VLE, \(PVT\), \(C_P\), and \(C_V\) properties of \(n\)-alkanols with an accuracy comparable, and for the near critical \(C_V\) data even higher, than that achieved with empirical multiparameter equations of state. The GC SAFT EOS not only gives excellent representation of the thermodynamic properties in the one-phase region but is also capable of reproducing the van der Waals loops in the two-phase region. The molecularly based, rather than empirical, nature of the GC SAFT EOS allowed us to incorporate the GC SAFT EOS into the generalized crossover DFT integrals,\(^16\) and thus develop a GC SAFT-DFT model for the surface tension of associating fluids. By incorporating the GC SAFT EOS into the crossover DMT equations obtained by Kiselev and Kulikov,\(^61,62\) we have also developed a GC SAFT-DMT model for the transport properties. The GC SAFT-DFT/DMT model has been tested against experimental surface tension, thermal conductivity, and thermal diffusivity data for methanol, ethanol, and butan-1-ol. In addition to the classical SAFT parameters, the GC SAFT-DFT/DMT model requires the asymptotic critical amplitude of the correlation length and the background contributions for the transport coefficients as input, and has proven to be very accurate. Except for the generalized crossover model for simple fluids developed recently by Kiselev and Ely,\(^17\) we are not aware of any other molecular or empirical models describing the thermodynamic, interfacial, and transport properties in pure fluids with comparable accuracy and physical self-consistency. The next step is applying this model to mixture calculations. Work in this direction is now in progress, and the results will be reported in future publications.

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