A new analytical formulation for the generalized corresponding states model for thermodynamic and surface properties in pure fluids

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Abstract

In a previous study [Kiselev, S.B., Ely, J.F., 2003. Generalized corresponding states model for bulk and interfacial properties of pure fluids and fluid mixtures. Journal of Chemical Physics 119(16), 8645–8662] we developed a formulation of the generalized corresponding states (GCS) model which incorporated critical region non-analytic behavior via a parametric crossover function. The parametric variable in that model was obtained from the crossover modification of the sine model originally proposed by Fisher et al. [1999. Trigonometric models for scaling behavior near criticality. Physical Review B 59(22), 14533–14545]. In this work we have developed a new version of the GCS model that incorporates an analytical sine (ANS) model solution which greatly simplifies the application of the resulting equation of state (EOS). Similar to the original GCS/CRS model, the new GCS/ANS model contains the critical point parameters and acentric factor as input and yields a very accurate description of the PVT- and VLE-surfaces of one-component fluids in a wide range of thermodynamic states, including the nearest vicinity of the critical point. The GCS/ANS model reproduces the saturated pressure and liquid density data with an average absolute deviation (AAD) of about 1% and the vapor density with AAD of about 2–3%. In the one phase region for $r < r_c$, the model reproduces the PVT data with an AAD less than 2% and for liquid densities where $r > r_c$ with an AAD of about 1–2%. In combination with the density functional theory (DFT), the GCS/ANS–DFT model is also capable of reproducing the surface tension of one-component fluids (polar and non-polar) with high accuracy.

Keywords: Interface; Phase equilibria; State equation; Supercritical fluid; Theory of liquids; Thermodynamic properties

1. Introduction

The cubic equation of state (EOS) first introduced by van der Waals (vdW) (van der Waals and Kohnstamm, 1927), is the simplest equation, which predicts the existence of the critical point and yields a qualitative prediction of vapor–liquid equilibrium in real fluids. It also allows an explicit formulation of the corresponding states (CS) principle. However, the quantitative difference between predictions of the vdW EOS and experiment in real molecular fluids is rather substantial, especially in the critical region. More recent modifications of the vdW EOS proposed by Redlich and Kwong (1949), Soave (1972), and Peng and Robinson (1976) amongst others, yield a much better representation of the thermodynamic properties

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molar classical Helmholtz free energy \( a(T, v) = A(T, v)/RT \) in two contributions

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

(1)

where the critical, \( \Delta a(\Delta T, \Delta v) \), and background, \( a_{bg}(T, v) \), parts are given by

\[
\Delta a(\Delta T, \Delta v) = a^{\text{res}}(\Delta T, \Delta v) - a_0^{\text{res}}(\Delta T) + \bar{P}_0(\Delta T)\Delta v - \ln(\Delta v + 1),
\]

(2)

\[
a_{bg}(T, v) = a_0^{\text{res}}(T) - \bar{P}_0(\Delta v)\Delta v + a_0^{id}(T),
\]

(3)

where \( \Delta T = T/T_0 - 1 \) and \( \Delta v = v/v_{0c} - 1 \) are dimensionless deviations of the temperature \( T \) and the molar volume \( v \) from the classical critical temperature \( T_0 \) and molar volume \( v_{0c} \), predicted by the classical EOS, \( \bar{P}_0(T) = P_0(T, v_{0c})v_{0c}/RT \) is the dimensionless pressure, \( a_0^{\text{res}}(T) = a^{\text{res}}(T, v_{0c}) \) is the dimensionless residual part of the Helmholtz energy along the critical isochore \( v = v_{0c} \), and \( a_0^{id}(T) \) is the dimensionless temperature-dependent ideal gas Helmholtz free energy.

In the second step, one replaces the classical values of \( \Delta T \) and \( \Delta v \) in the critical part \( \Delta a(\Delta T, \Delta v) \) with the renormalized values (Belyakov et al., 1997; Kiselev and Ely, 2001)

\[
\tau = \tau' \Gamma^{-x/2}\Delta t + (1 + \tau') \Delta t, \quad \gamma = \gamma'/2\beta + \gamma_0 - 1.
\]

(4)

\[
\eta = \eta' \Gamma^{-x/2}\Delta t + (1 + \eta) \Delta t', \quad \gamma = \gamma'/2\beta + \gamma_0 - 1,
\]

(5)

where \( x = 0.11, \beta = 0.325 \), and \( \gamma = -2 - 2\beta - x = 1.24 \) are universal non-classical critical exponents (Albright et al., 1986; Anisimov and Kiselev, 1992) \( \tau = T/T_c - 1 \) is a dimensionless deviation of the temperature from the true critical temperature \( T_c \), \( \eta = v/v_{0c} - 1 \) is a dimensionless deviation of the molar volume \( v \) from the true critical molar volume \( v_{0c}, \Delta T_c = (T_c - T_0)/T_0 \ll 1 \) and \( \Delta v_c = (v - v_{0c})/v_{0c} \ll 1 \) are dimensionless shifts of the critical temperature and volume, and \( \Gamma(q) \) is a crossover function (Belyakov et al., 1997; Kiselev and Ely, 2001).

Since the RG equations cannot be solved analytically, no rigorous theoretical expression for the crossover function can be obtained. Therefore, in practice, different approximants are used for the crossover function \( \Gamma \). The simplest one is a phenomenological expression obtained by Kiselev (1998)

\[
\Gamma(q) = \left( \frac{q}{1 + q} \right)^{2\Delta t},
\]

(6)

where \( q = (r/Gi)^{1/2} \) is a renormalized distance to the critical point \( r(T, \eta) \) is a parametric variable. The crossover function \( \Gamma \) as given by Eq. (6) coincides with the corresponding RG-theory crossover function obtained in the first order of \( e \)-expansion by Belyakov and co-workers (Belyakov et al., 1997). Initially, the renormalized distance \( q \) was found by Kiselev and co-workers from a solution of the crossover linear model (LM) (Kiselev, 1998; Kiselev and Ely, 1999; Kiselev and Friend, 1999). In our more recent works, we found \( q \) from a solution of the crossover sine (CRS) model (Kiselev and Ely, 2000, 2003, 2004; Kiselev et al., 2000, 2001)

\[
\left( q^2 - \frac{\tau}{Gi} \right) \left[ 1 - \frac{p^2}{4b^2} \left( 1 - \frac{\tau}{q^2} \right) \right] = b^2 \left( \frac{\eta(1 + v_1 \exp(-10\eta)) + d_1\tau^2}{m_0Gi\beta} \right)^2 \Gamma^{(1-2\beta)/\Delta t},
\]

(7)

where \( m_0, v_1, d_1, \) and \( Gi \) are system-dependent parameters, while the universal parameters \( p^2 = b^2 \) can be set equal to the LM parameter \( b_{LM} = 1.359 \). The CRS model, unlike the crossover LM, can be extended into the metastable region and at temperatures \( T < T_c \) gives analytically connected vDW loops. The term \( \propto d_1 \tau \) in Eq. (7) corresponds to the rectilinear diameter of the coexistence curve, which appears from the cubic term in the Landau expansion (Landau and Lifshitz, 1980; Patashinskii and Pokrovski, 1979). The LM crossover equation for the parametric variable \( q \) employed earlier by Kiselev et al. (Kiselev, 1990, 1997; Kiselev and Rainwater, 1998; Kiselev and Sengers, 1993) is recaptured from Eq. (7) when parameter \( p^2 \to 0 \). Finally, a crossover expression for the Helmholtz free energy can be written in the form

\[
\bar{a}(T, v) = \Delta a(\bar{\tau}, \bar{\eta}) - \Delta v\bar{P}(T) + a_0^{\text{res}}(T) + a_0^{id}(T).
\]

(8)

The crossover EOS can be obtained by differentiation of Eq. (8) with respect to the volume

\[
P(v, T) = -RT\frac{\partial \bar{a}}{\partial v} = -RT \omega_{0c} \left( \frac{\partial \Delta a}{\partial \eta} \right) - \bar{P}(T).
\]

(9)

In our previous work (Kiselev and Ely, 2003), we used this approach to develop a generalized CS model with crossover (GCS/CRS), that contains only the critical parameters and acen- tric factor as input but accurately reproduces the PVT- and VLE-surfaces and the surface tension of one-component fluids (polar and non-polar) in a wide range of thermodynamic states, including the nearest vicinity of the critical point. However, since Eq. (7) is a transcendental equation with respect to \( q \), it can only be solved numerically. This makes the calculation of the crossover function and its first and second derivatives with respect to the temperature, density, and composition complicated and restricts its widespread practical application for engineering calculations. In order to overcome this shortcoming of the GCS/CRS model, we develop here a fully analytical formulation for the crossover function that can be used in the GCS and other models.

We proceed as follows: in Section 2 we describe an analytical sine model (ANS) for the crossover function \( \Gamma \). In Section 3, we present a redefined formulation for GCS model and provide its comparison with experimental VLE, PVT, and surface data for pure fluids. Our results are summarized in Section 4.

2. Analytical sine model

Far away from the critical point \( q \to \infty \), the crossover function \( \Gamma \to 1 \) and the renormalized temperature \( \bar{\tau} = \tau + (1 + \tau)\Delta T_c = T/T_0 - 1 \) and order parameter \( \bar{\eta} = \eta + (1 + \eta)\Delta v_c = v/v_{0c} - 1 \) coincide with their classical values \( \Delta T \)
and \( \Delta v \). Thus, in this limit the crossover expression for the Helmholtz free energy, Eq. (8) is always transformed to its classical analog, Eq. (1). Therefore, in order to develop an ANS model, which reproduces an asymptotic scaling behavior in the critical region, one needs to first consider the asymptotic behavior of the crossover function as \( q \to 0 \).

Asymptotically close to the critical point at \( q \ll 1 \), and the crossover function becomes

\[
\Upsilon(q) \approx q^{2d_1} = \left( \frac{r}{G_i} \right)^{d_1}.
\]

(10)

Thus, Eq. (7) is transformed into the trigonometric model originally developed by Fisher and co-workers (Fisher et al., 1999)

\[
\tau = r \left( 1 - 2b \frac{1 - \cos(p\theta)}{p^2} \right), \quad \eta = m_0 r^\beta \sin(p\theta) / p,
\]

(11)

and in the case \( p^2 = b^2 \)

\[
(r - \tau) \left[ 1 - \frac{1}{4} (r - \tau) \right] = \left( \frac{b}{m_0} \right)^2 r^{2-2\beta},
\]

(12)

where we have introduced a notation \( \tilde{\eta} = \eta[1 + v_1 \exp(-10\eta)] + d_1 r \). Along the critical isochore (\( \tilde{\eta} = 0 \)) Eq. (12) has a solution \( r = \tau \) when \( \tau > 0 \) and \( r = |\tau|/3 \) when \( \tau < 0 \), and along the critical isotherm (\( \tau = 0 \)) its solution is given by

\[
r = \left( \frac{4b}{3m_0} \tilde{\eta} \right)^{1/\beta}.
\]

(13)

Eq. (12) does not contain the crossover function \( \Upsilon \) and, therefore, is simpler than Eq. (7). However, it is still a transcendental equation with respect to \( r \) and can only be numerically solved for arbitrary \( \tau \) and \( \eta \). In order to overcome this shortcoming, we rewrite Eq. (12) in the form

\[
(r - \tau) \left[ 1 - \frac{1}{4} (r - \tau) \right] = \left( \frac{b}{m_0} \tilde{\eta} \right)^a r^{2-b},
\]

(14)

and set \( a = 1/\beta \) and \( b = 1 \). Given this notational change, Eq. (14) can be rewritten in the form

\[
3r^2 - r \left[ 4 \left( \frac{b}{m_0} \tilde{\eta} \right)^{1/\beta} + 2\tau \right] - \tau^2 = 0,
\]

(15)

with the solution

\[
r = \frac{4((b/m_0)\tilde{\eta})^{1/\beta} + 2\tau + \sqrt{[4((b/m_0)\tilde{\eta})^{1/\beta} + 2\tau]^2 + 12\tau^2}}{6}.
\]

(16)

Along the critical isochore (\( \tilde{\eta} = 0 \)), the solution of Eq. (15) exactly coincides with corresponding solutions of Eq. (12), while along the critical isotherm, \( \tau = 0 \), the solution reads

\[
r = \frac{4}{3} \left( \frac{b}{m_0} \tilde{\eta} \right)^{1/\beta}.
\]

(17)

If we perform the renormalization \( m_0 \to m_0(3/4)^{1-\beta} \), this result also coincides with the corresponding solution of the original sine model, Eq. (13).

Finally, the parametric variable \( q \) in Eq. (6) for the crossover function \( \Upsilon(q) \) in the ANS model can be written in the form:

\[
q^2 = \frac{4((b/m_0)\tilde{\eta})^{1/\beta} + 2\tau + \sqrt{[4((b/m_0)\tilde{\eta})^{1/\beta} + 2\tau]^2 + 12\tau^2}}{6Gi}.
\]

(18)

It easy to show that when \( \tau < 0 \) (or \( T < T_c \)) the ANS model predictions as given by Eqs. (6) and (18) are very similar to the CRS model and can be extended into the metastable region where \( |\eta| \leq |\rho_p/\rho_{v,L} - 1| \) (or \( \rho_p(T) \leq \rho \leq \rho_{v,L}(T) \)).

A comparison of the crossover function \( \Upsilon(q) \) calculated with the parameter \( q \) defined from the CRS model (Eq. (7) with \( v_1 = d_1 = 0 \) (or \( \tilde{\eta} = \eta = \rho_p/\rho - 1 \)), \( Gi = 0.01 \), and \( m_0 = 1 \) and from the ANS model (Eq. (18) with \( m_0 = 1.2 \)) is shown in Fig. 1. As one can see, along the critical isochore \( \eta = 0 \) and along the critical isotherm \( \tau = 0 \) at \( \eta \ll 1 \), the two crossover functions are practically indistinguishable, thus providing a correct renormalization of all thermodynamic properties in the asymptotic critical region where \( q \ll 1 \). Far away from the critical point (at \( q \gg 1 \), or at \( \eta > 10 \) and \( \tau > 1 \)), both crossover functions approach unity as they must in order to approach the ideal gas state. However, there are some systematic deviations between these two crossover functions in the intermediate-crossover region where 0.05 < \( \eta \ll 1 \) and \( \tau < 1 \) (or 0.1 < \( q < 10 \)). This means, that if one were to switch from the full crossover model (CRS) to the analytical (ANS) model, all system-dependent parameters, namely the coefficients \( m_0, v_1, d_1 \), and the Ginzburg number \( Gi \), should be redefined.

3. Redefined GCS model

The GCS model developed in our previous work (Kiselev and Ely, 2003), was based on the analytical–classical cubic
Patel–Teja (PT) EOS (Patel, 1996; Patel and Teja, 1982) and the CRS model for the crossover function $\Upsilon(q)$, Eqs. (6) and (7). In this work, we reformulated the GCS model by using the ANS model defined by Eq. (18) for $\Upsilon(q)$. The differences between CRS and ANS models in the intermediate range of the parameter $q$, force us to redefine the CS correlations for the classical compressibility factor $Z_c$, the parameters $v_1$, $d_1$, $m_0$, the Ginzburg number $G_i$ that were reported in our previous work (Kiselev and Ely, 2003).

Following the methods used to develop the GCS/CRS model, we set $T_{0c} = T_c$ (or $\Delta T_c = 0$ in Eq. (4)). Then, using a procedure described in our previous work, we found that the parameter $m_0$ for the GCS/ANS model can be also considered as a system-independent constant, $m_0 = 2.5$, while for the classical compressibility factor $Z_c$, and the coefficients $v_1$ and $d_1$ can be represented as simple linear functions of the real compressibility factor $Z_c$:

$$Z_c = \begin{cases} 0.080227 + 0.879825Z_c, & Z_c < Z_c^{\text{max}}, \\ 0.333333, & Z_c \geq Z_c^{\text{max}} = 0.287672, \end{cases}$$

$$d_1 = 13.7932 - 52.8651Z_c,$$

$$v_1 = -0.022223 + 0.125625Z_c.$$  

For the Ginzburg number in the GCS/ANS model we adopted the same expression as in the GCS model, but with redefined
one phase region where 1% and the vapor density with an AAD of about 2–3%. In the reproduction of the saturated pressure and liquid density data for each other. Like the GCS/CRS model, the GCS/ANS model in Figs. 2 and 3. As one can see, in all cases the GCS/ANS experimental data and the predictions of the GCS/CRS model in the metastable region at temperatures

\[ f^{\text{ANS}}(T_r, \rho_r; \omega, Z_c), \]

where, however, instead the GCS/CRS crossover function \( f^{\text{CR}} \) we now use the ANS model crossover function \( f^{\text{ANS}} \). An exact analytical expression for \( f^{\text{ANS}} \) can be obtained from Eqs. (8) and (9), where for the classical residual Helmholtz free energy one should use an analytical expression obtained from the integration of the cubic PT EOS

\[ \sigma^{\text{res}}(T, \nu) = -\frac{1}{RT} \int P_{\text{PT}}(T, \nu) \, d\nu + a_0(T). \]

Since all derivatives \( \partial^2 \gamma / \partial \nu \), \( \partial^2 \gamma / \partial \nu^2 \), \( \partial^2 \gamma / \partial \tau \partial \eta \), and \( \partial^2 \gamma / \partial \tau^2 \partial \eta \) in the ANS model can be taken analytically, the corresponding derivatives of the crossover function \( f^{\text{ANS}} \) and, consequently, of the pressure \( P(T, \nu) \) with respect to the temperature, \( T \), and density, \( \rho = 1/\nu \), can be obtained in a closed analytical form. This makes the GCS/ANS model much more convenient for the practical applications than the GCS/CRS model.

The predictions of the GCS/ANS model for water, carbon dioxide, and some hydrofluorocarbons are compared with experimental data and the predictions of the GCS/CRS model in Figs. 2 and 3. As one can see, in all cases the GCS/ANS and GCS/CRS predictions either coincide, or lie very close to each other. Like the GCS/CRS model, the GCS/ANS model reproduces the saturated pressure and liquid density data for all fluids with an average absolute deviation (AAD) of about 1% and the vapor density with an AAD of about 2–3%. In the one phase region where \( \rho \leq 2 \rho_c \), the GCS model reproduces the PVT data with an AAD less than 2% and for liquid densities where \( \rho \geq 2 \rho_c \), with an AAD of about 1–2%.

Fig. 2 shows that the GCS/ANS model as well as the GCS/CRS model generates analytically connected vdW loops in the metastable region at temperatures \( T < T_c \). This allows us to use the GCS/ANS model in the density functional theory (DFT) expression for the surface tension (Kiselev and Ely, 2003)

\[ \sigma = c_0^{1/2} \int_{\rho_v}^{\rho_L} \left[ \Delta A(\rho) \right]^{1/2} d\rho, \]

where \( \Delta A(\rho) = \rho A_v(T, \rho) - \rho A(T, \rho_{\nu, L}) = \rho RT \Delta a(T, \rho) \) is the excess part of the Helmholtz free energy density, and \( \mu(T, \rho_{\nu, L}) = (\partial \rho A / \partial \rho)_{T, \nu} \) is the chemical potential of the bulk fluid along the saturated curve \( \rho = \rho_{\nu, L}(T) \).

In this work, we have used Eq. (8) with all parameters obtained from the GCS/ANS model for the calculation of the excess free energy density \( \Delta A(T, \rho) \) that appears in Eq. (25).

Using the methods from the development of the GCS/CRS–DFT, for ordinary and heavy water we set

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

where \( k_B \) is Boltzmann’s constant, and for all other fluids

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

For the parameter \( \kappa_0 \) in Eqs. (26) and (27) we use the relation

\[ \kappa_0 = 0.141782 M_w (1 - 3.31649 Z_c - 0.3545 \omega), \]
which differs from the corresponding expression in the
GCS/CRS–DFT model (Kiselev and Ely, 2003).

A comparison of the GCS/ANS–DFT predictions for the
surface tension with experimental data for water is shown in
Fig. 4. The solid curves in Fig. 4 correspond to the values
calculated with the GCS/CRS–DFT with the experimental
values of the parameter \( \kappa_0 = 0.33 \) (Kiselev and Ely, 2003),
while the dashed curves represent the GCS/ANS predic-
tions with the parameter \( \kappa_0 \) determined from Eq. (28).
In the entire temperature range from the critical temperature to
\( T = 400 \) K, good agreement between experimental data and
GCS/ANS predictions is observed. At temperatures \( T < 400 \) K,
the GCS/ANS predictions lie systematically lower than experi-
mental data. But even at low temperatures the deviations from experimental data do not exceed 7%, which can be con-
sidered to be excellent predictions in a fluid as complex as
water. The GCS/ANS–DFT predictions are compared with sur-
face tension data for methane, ethane, and carbon dioxide in
Fig. 5. Again, excellent agreement between GCS/ANS–DFT and
experimental data for all fluids is observed.

4. Conclusion

A general phenomenological procedure for transformation of
any classical equation into the crossover form, which in
the critical region reproduces theoretically well established
scaling laws, and in the limit of low densities is transformed
into the ideal gas equation was proposed by Kiselev (1998).
In this work, using this procedure and a new ANS model
for the crossover function, we developed a new formulation
for the GCS model, which uses the Patel–Teja (PT) EOS
(Patel and Teja, 1982) as a reference EOS for one-component
fluids. Unlike the GCS model developed before (Kiselev
and Ely, 2003), the new GCS/ANS model is fully analytical and
does not require a numerical solution of any transcendental
equation. When \( T > T_c \) and \( \rho < 1.8 \rho_c \), the GCS/ANS model
reproduces the pressures and, when \( \rho > 1.8 \rho_c \), the liquid
densities with an AAD of about 1–2%. In the temperature region
\( T \lesssim T_c \), the new GCS/ANS reproduces the saturated pressure
data with an AAD of about 0.5–1%, the liquid density data with
an AAD of about 1%, and the vapor density to within 2–3%.
In combination with the DFT, the GCS/ANS–DFT model
also yields an excellent description of the surface tension of
one-component fluids.

In present work, we considered the GCS with a simple cubic
PT EOS as an example. In principle, the same approach, i.e.,
replacement of the CRS model employed before (Kiselev and
Ely, 2003) with the new ANS model, can be also be applied
to other types of crossover equations including SAFT (Hu
et al., 2003a; Kiselev and Ely, 1999; Kiselev et al., 2001), SAFT-
BACK (Hu et al., 2003b), SAFT-VR (McCabe and Kiselev,
2004a,b), and structure optimized empirical multi-parameter
equations of state (Sun et al., 2005). Of course, all system-
dependent parameters in these equations must be redefined.
Similar to the GCS model, the GCS/ANS can be also extended
to binary mixtures. Work in this direction is now in progress,
and the results will be reported in future publications.

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