Incorporating Critical Divergence of Isochoric Heat Capacity into the Soft-SAFT Equation of State

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In the critical region, widely used equations of state, including molecular-based statistical associating fluid theory (SAFT) equations, fail to quantitatively describe the critical anomalies affected by the diverging fluctuations of density due to their classical mean-field approximation. Description of some properties in the critical region, in particular vapor-liquid coexistence and isothermal compressibility, can be improved by fitting (multi) parameters of an equation of state to the properties obtained in accurate computer simulations. However, some anomalies in the critical region, which are caused exclusively by critical fluctuations, cannot be readily generated by this procedure. An example of a critical anomaly, completely absent in the mean-field approximation, is the divergence of the isochoric heat capacity. A simplified methodology for modifying the original soft-SAFT equation of state to take into account these anomalies is explored. Possible procedures for further improvement are mentioned.
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Introduction

An accurate knowledge of the thermodynamic properties of fluids and fluid mixtures is a matter of primary concern for many industrial processes, representing a key issue in process design. Scientifically based thermodynamic equations have the advantage that they can be applied to a compound at thermodynamic conditions for which limited experimental information is available. Among many areas of interest, new industrial technologies use a wide variety of fluid-separation processes where critical conditions are encountered. Classical equations of state are commonly used because of their simplicity and their accurate description of the thermodynamic properties of fluids far from the critical point.[1–3] However, they fail in the near-critical region, as they do not account for the actual asymptotic nonanalytic critical behavior of the thermodynamic properties due to critical fluctuations of the density.

The asymptotic thermodynamic behavior of fluids is characterized by universal scaling laws with universal exponents[4,5] in accordance with the modern renormalization-group theory of critical phenomena.[6] To incorporate the correct critical scaling behavior into equations of state, one needs a theory that explicitly accounts for a crossover from nonanalytic fluctuation-induced asymptotic critical behavior to classical analytic behavior farther away from the critical point, where density fluctuations become negligibly small. Several approaches toward this goal have been pursued in the literature, as reviewed by Behnejad et al.[5] One such approach is a renormalization of a classical Landau expansion originally proposed by Chen et al.[7,8] and further developed by Anisimov et al.[9] with a phenomenological variant proposed by Kiselev.[9–11] Another major approach is a numerical implementation of a renormalization procedure in the so-called phase-space cell approximation, originally developed by White and coworkers.[12–14] Both approaches have been used to improve the representation of thermodynamic properties of fluids and fluid mixtures in the critical region. Again, a comprehensive list of references can be found in Behnejad et al.[5] Among others, the numerical renormalization procedure of White was applied by Prausnitz and coworkers, who were the first to identify some of the approximations that the theory requires for practical implementation, to represent the thermodynamic properties of *n*-alkanes,[15,16] extending the method to binary mixtures[17–19] and even to multicomponent mixtures.[20] An appropriate equation of state, able to reproduce the thermodynamic properties of a fluid accurately, is a key requirement for successful modeling. For this purpose, model equations of state based on statistical mechanics have several advantages over empirical phenomenological equations of state: (a) the observed properties are directly related to the underlined molecular model, (b) if the agreement between experimental data and the model is not acceptable, this can be improved systematically, and (c) the models can be used to investigate the effect of the different variables in an independent way. Among equations with a

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molecular-based approach, the most successful one is the statistical associating fluid theory (SAFT).[2,21,22] The theoretical basis of SAFT has recently been reviewed by McCabe and Galindo.[2] SAFT equations have been successful in providing quantitative predictions of thermodynamic properties and phase behavior in a large number of systems for industrial application. However, being classical mean-field equations, they still become inadequate in the near-critical region.

Several attempts have been made to improve SAFT equations of state in the critical region with the help of the two major approaches for dealing with the crossover critical behavior mentioned above. Specifically, Kiselev et al. have used their phenomenological versions of a renormalized Landau expansion to develop crossover SAFT,[23–26] crossover SAFT-VR,[27,28] and SAFT-VRX[28–30] equations of state. This approach has also been used by Hu et al.[31,32] White's numerical renormalization procedure in the phase-space cell approximation has been applied by different authors to several versions of SAFT equations of state, such as the original SAFT,[33,34] the soft-SAFT,[35–38] the SAFT-VR,[39,40] and the PC-SAFT.[41,42] However, both approaches have some short comings.

First, the renormalized Landau expansion in the formulation of Kiselev and coworkers accounts for the corrections to a mean-field equation of state in the absence of critical fluctuations. In practice, SAFT equations contain a number of coefficients determined by comparison either with computer simulations or with experimental data. Hence, depending on the SAFT version used and the data employed, these parameters already account for some effects of critical fluctuations. As a consequence, one of the problems of incorporating such a renormalization procedure into a multiparameter SAFT equation is that the contributions from critical fluctuations may be overcorrected. Although not intrinsic of the renormalized Landau expansion, an additional limitation of the phenomenological version proposed by Kiselev, is the number of adjustable parameters (typically three or more), preventing the treatment to be used in a transferable manner.

To appreciate the limitations of a numerical renormalization procedure in the phase-space cell approximation, one should distinguish between strongly divergent thermodynamic properties, like the isothermal compressibility, κ_T, which already diverges in the mean-field approximation, albeit with an incorrect critical exponent, and weakly divergent thermodynamic properties, like the isochoric heat capacity, C_V, that do not diverge at all in the mean-field approximation. Physically, the strong divergence of the isothermal compressibility κ_T is caused by the long-range nature of the radial distribution function $g(r)$ for large values of the distance r, as $k_\mathrm{B}T\kappa_T=\rho^2\int d\mathbf{r}\, g(r)$, where k_B is the Boltzmann's constant, T is the temperature, and ρ the number density.[43,44] In contrast, the configurational internal energy U is related to the radial distribution function by[45,46] $U=\frac{1}{2}N\rho\int d\mathbf{r}\varphi(r)\, g(r)$, where N is the number of molecules, and $\varphi(r)$ is the intermolecular potential, which is short range. Hence, the critical behavior of the internal energy, and of its temperature derivative, is determined by the effect of the critical fluctuations on the short-range behavior of the radial distribution function.[47] In the theory of critical phenomena, it means that the renormalization of a classical Landau expansion not only involves a rescaling of the physical variables, but also involves an additive renormalization term, commonly referred to as the kernel term, responsible for the divergent behavior of the isochoric heat capacity.[7,8] The numerical renormalization procedure in the phase-space cell approximation accounts for the long-range behavior of the density correlation function, but has not been very successful in describing the divergent behavior of the isochoric heat capacity caused by the more subtle short-range effects of the critical fluctuations on the correlation function near the critical point.[48]

The purpose of the present contribution is to investigate whether the critical divergence of the isochoric heat capacity can be better accounted for by a phenomenological method consisting of adding a kernel term to SAFT, whose presence is predicted by the renormalization-group theory of critical phenomena.[7] Specifically, we shall consider here the soft-SAFT equation of state, which uses a Lennard-Jones (LJ) model to describe the interaction between monomers,[2,49,50] in contrast to the hard-sphere interaction in the original version. The predictive power and accuracy of soft-SAFT has been checked with experimental systems for which cubic-type equations of state fail.[51–53] The research group of Vega and coworkers has broad expertise in developing and applying the soft-SAFT approach to deal with thermodynamic properties and phase equilibria of fluids and fluid mixtures.[35–38,54–56] In particular, Vega and coworkers[35–38] have performed a numerical implementation of the renormalization procedure of White and coworkers into the soft-SAFT equation, usually called crossover soft-SAFT. The extended equation captures the asymptotic thermodynamic behavior as one approaches the critical point. However, some limitations regarding the numerical implementation of the multiparameter SAFT equation were observed. In particular, crossover soft-SAFT was unable to accurately predict the divergence of the isochoric heat capacity.[37]

We shall proceed as follows. We first formulate the soft-SAFT equation of state to be considered. We then elucidate the nature of a kernel term predicted from the theory of critical phenomena and how a simplified version can be added to the soft-SAFT equation of state. The soft-SAFT equation of state is then tested for argon as a representative simple example. We conclude this contribution with a discussion of the results and a recommendation for possible further research.

Theory

The soft-SAFT equation of state

Soft-SAFT,[54] as any other SAFT-type equations of state, is expressed in terms of the Helmholtz energy. In the SAFT approach, the Helmholtz energy A of a homogeneous fluid is written as a perturbation expansion, which takes into account molecular interactions of different origin. In the case of associating molecules, the Helmholtz energy can be expressed as a sum of an ideal contribution A^ideal, a reference term A^ref, which takes into account the attractive and repulsive forces between spherical molecules (or monomers/segments making a chain), a chain contribution A^chain, which accounts for the connectivity of the segments in the molecules, and a contribution due to site-site intermolecular association A^assoc.[2,54] The residual Helmholtz energy of the reference system, defined as $A^\mathrm{res}=A^\mathrm{total}-A^\mathrm{ideal}$, is expressed as

$$\frac{A^\mathrm{res}}{Nk_\mathrm{B}T}=\frac{A^\mathrm{ref}}{Nk_\mathrm{B}T}+\frac{A^\mathrm{chain}}{Nk_\mathrm{B}T}+\frac{A^{\mathrm{asso}c}}{Nk_\mathrm{B}T} \tag{1}$$

The ideal term is given in the standard form as[2]

$$\frac{A^{\text{ideal}}}{Nk_{\text{B}}T}=\ln\left(\rho\Lambda_{\text{DB}}^{3}\right)-1 \tag{2}$$

where Λ_{DB} is the thermal de Broglie wavelength which contains the translational and rotational contributions to the partition function of the ideal-gas fluid.

Soft-SAFT uses a LJ intermolecular potential, with well depth ε and diameter σ, as a reference term that accounts for the repulsive and attractive interactions of the monomers forming the chain. We use the expression of Johnson et al.,[49] fitted to LJ fluid simulation data for a wide range of reduced temperatures and densities, to specify the reference term

$$\frac{A^{\text{ref}}}{Nk_{\text{B}}T}=\varepsilon_{ii}\left(\sum_{p=1}^{8}\frac{a_p(T)}{p}\left(\rho_{\text{m}}^{\text{ref}}\right)^{p}+\sum_{p=1}^{6}b_p(T)G_p\left(\rho_{\text{m}}^{\text{ref}}\right)\right) \tag{3}$$

In Eq. 3, $a_p(T)$ and $b_p(T)$ are functions of temperature. These functions contain 32 linear parameters of a Modified Benedict–Webb–Rubin equation type.[49] The function $G_p(\rho_{\text{m}}^{\text{ref}})$ contains exponentials of the reference (monomeric) density $\rho_{\text{m}}^{\text{ref}}$ of the LJ cores, which is related to the number density ρ by the number m of segments (LJ spheres) of the chain ($m=1$ for the LJ case) and by the segment diameter σ as $\rho_{\text{m}}^{\text{ref}}=m\rho\sigma^3$. The chain and association contributions are formally identical in the different versions of SAFT.[2] In soft-SAFT, the chain term is obtained as a function of the chain length m and of g_{LJ}, the radial distribution function of a fluid of LJ spheres at the density $\rho_{\text{m}}^{\text{ref}}$

$$\frac{A^{\text{chain}}}{Nk_{\text{B}}T}=(1-m)\ln g_{\text{LJ}} \tag{4}$$

To obtain g_{LJ}, we use the expression adopted by Johnson et al. and fitted to computer simulation data of LJ spheres at contact as a function of temperature and density.[50] Finally, the association contribution for M associating sites on a molecule is obtained from the thermodynamic perturbation theory of Wertheim[57–59]

$$\frac{A^{\text{assoc}}}{Nk_{\text{B}}T}=\sum_{a}\left(\ln X_a-\frac{X_a}{2}\right)+\frac{M}{2} \tag{5}$$

where X_a is the fraction of unbonded molecules to a site of type a and M is the total number of association sites. The value of X_a comes from the solution of the following mass-action equation

$$X_a=\frac{1}{1+\rho\sum_{b=1}^{s}X_b\Delta_{ab}} \tag{6}$$

where the specific site-site function, Δ_{ab}, is approximated as

$$\Delta_{ab}=K_{ab}^{\text{HB}}f_{ab}g_{\text{LJ}} \tag{7}$$

Equation 7 includes two additional molecular parameters for associating molecules: K_{ab}^{HB}, related to the site-site bonding-volume of association, and the site-site association energy $\varepsilon_{ab}^{\text{HB}}$, included in the Mayer f-function[2]: $f_{ab}=\left[\exp\left(\frac{\varepsilon_{ab}^{\text{HB}}}{k_{\text{B}}T}\right)-1\right]$. The association term is solved by a generalized numerical procedure proposed by Tan et al.[60]

Incorporating a divergent isochoric heat capacity

We introduce dimensionless thermodynamic quantities, reduced by the critical parameters (denoted by the subscript c)

$$\begin{aligned}&\overline{T}=\frac{T}{T_{\text{c}}},\ \overline{\rho}=\frac{\rho}{\rho_{\text{c}}},\ \overline{P}=\frac{P}{\rho_{\text{c}}k_{\text{B}}T_{\text{c}}},\ \overline{\mu}=\frac{\mu}{k_{\text{B}}T_{\text{c}}},\ \overline{A}=\frac{\rho A}{\rho_{\text{c}}Nk_{\text{B}}T_{\text{c}}},\\&\overline{C}_V=\frac{\rho C_V}{\rho_{\text{c}}Nk_{\text{B}}},\ \overline{\chi}=\frac{k_{\text{B}}T_{\text{c}}}{\rho_{\text{c}}}\chi\end{aligned} \tag{8}$$

where P is the pressure, μ the chemical potential per molecule, C_V the isochoric heat capacity, $\chi=(\partial\rho/\partial\mu)_T=\rho^2\kappa_T$ the isothermal susceptibility, and κ_T the isothermal compressibility.[9] In addition, dimensionless differences between the temperature and density and their critical values are defined as

$$\Delta\overline{T}=\frac{T-T_{\text{c}}}{T_{\text{c}}}\ \text{ and }\ \Delta\overline{\rho}=\frac{\rho-\rho_{\text{c}}}{\rho_{\text{c}}} \tag{9}$$

A theory for nonasymptotic critical thermodynamic behavior has been obtained in terms of a crossover Landau model in previous work.[7–9] In this theory, the variables $\Delta\overline{T}$ and $\Delta\overline{\rho}$ of the classical Helmholtz-energy density are renormalized in such a way that the vapor-liquid coexistence and the P, V, T properties satisfy the universal scaling-law behavior in the asymptotic vicinity of the critical point. In addition, a new (exclusively fluctuation-induced) contribution, called "kernel term" is added to account for the divergence of the isochoric heat capacity. Two coefficients of the rescaling of the temperature and density variables, respectively, specify the amplitudes of the thermodynamic power laws asymptotically close to the critical point.[61] The nonasymptotic crossover critical behavior is determined by two physical crossover parameters: a reduced coupling constant $\overline{u}$, related to the range of the intermolecular interactions, and a dimensionless wavenumber Λ, related to the cutoff wavenumber of the critical fluctuations.[61] The validity of this theory of crossover critical behavior has been confirmed by a comparison with numerical computer-simulation data for Ising models with different values for the coupling constant $\overline{u}$,[62] and with experimental data for polymer solutions with various values of Λ, related to the inverse of the radius of gyration of the polymer molecules.[63,64] The crossover Landau model has been used to represent the thermodynamic properties of many fluids in the critical region,[5] including argon.[65]

The reference term of soft-SAFT already partially accounts for the effects of the critical fluctuations in an empirical manner, because the P, V, T data obtained by simulations of the LJ reference fluid in the critical region are included in the parameter optimization.[49] Because of this, it is possible to obtain an acceptable description of the liquid-vapor coexistence for simple fluids, such as argon or methane consisting of spherical or quasi-spherical molecules, without any specific treatment. However, the description of some other properties, notably the adiabatic compressibility and the isochoric heat capacity, cannot readily be improved by this procedure since their anomalies do not exist in the mean-field approximation.

In this work, we consider the option of adding only the kernel term of the renormalization theory for critical phenomena to the original soft-SAFT given by Eq. 1, assuming that the P, V, T properties are represented by the original equation of state with acceptable quality. The modified equation is to be rewritten in terms of the reduced Helmholtz-energy density $\overline{A}$

$$\overline{A}=\overline{A}^{\text{res}}+\overline{A}^{\text{ideal}}=\overline{A}^{\text{ref}}+\overline{A}^{\text{chain}}+\overline{A}^{\text{assoc}}+\overline{A}_{\text{K}} \tag{10}$$

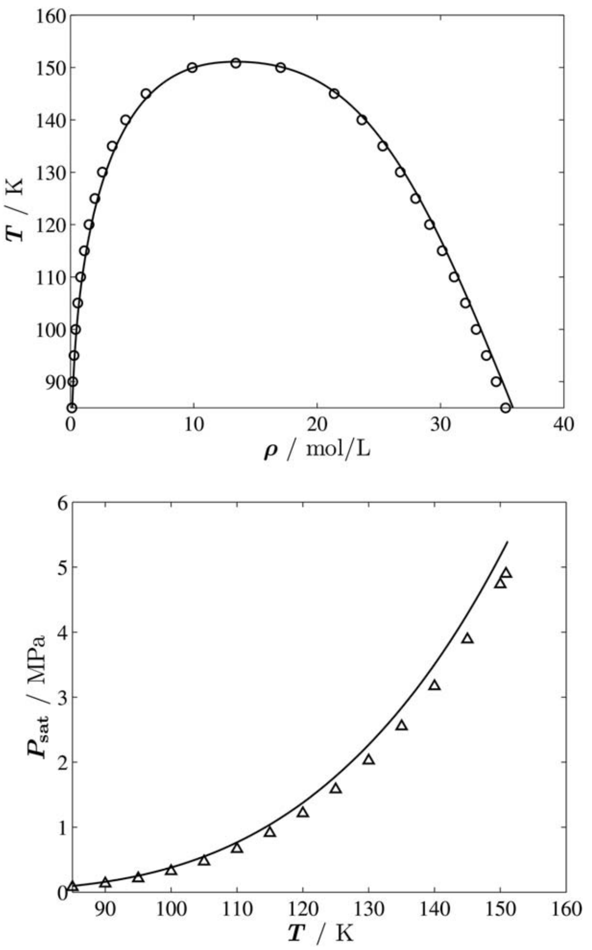

Figure 1. Top: Coexistence vapor-liquid equilibria curve of argon. Bottom: Saturation pressure of argon as a function of temperature.

The symbols indicate values from the NIST database.[71] The curves represent values calculated from soft-SAFT.

The kernel term in Eq. 10 is given by[61,62]

$$\overline{A}_{\mathrm{K}} = -\frac{1}{2}\phi\left(c_t\Delta\overline{T}\right)^2\mathscr{K} \tag{11}$$

where c_t is the rescaling coefficient of the temperature variable $\Delta\overline{T}$ and ϕ is an empirical function of density, introduced in this work, and chosen as $\phi=2\overline{\rho}/(1+\overline{\rho})$ to ensure convergence of the kernel term to zero in the limit $\rho\rightarrow 0$. In Eq. 11, $\mathscr{K}$ is a rescaling function expressed as[61,62]

$$\mathscr{K} = \frac{\nu}{\alpha\overline{u}\Lambda}\left(Y^{-\alpha/\Delta}-1\right) \tag{12}$$

where Y is a crossover function, $\alpha = 0.11$ and $\nu = 0.63$ are universal critical exponents characterizing the power-law divergence of the isochoric heat capacity and the correlation length of critical fluctuations along the critical isochore, respectively. Δ is a "correction-to-asymptotic-scaling" exponent, and $\overline{u}$ and Λ are system-dependent crossover parameters,[62] as already mentioned above. The values for α and ν have been established with high accuracy.[4] The value of Δ is known less accurately (0.5–0.52)[66] and has been fixed at 0.5. The "cutoff" parameter Λ is inversely proportional to the size of the molecules. In the lattice-gas model, $\Lambda = 1$.[62] The parameter $\overline{u}$ (coupling constant) varies for fluids and fluid mixtures between approximately[67] 0.5 and 1.5 and is fixed in this work at $\overline{u}=1$. The latter choice simplifies the form of the crossover function, which then depends only on the "distance" to the critical point, namely the function $\kappa(\Delta\overline{T},\Delta\overline{\rho})$, inversely proportional to the correlation length. In this approximation[63]

$$Y(\kappa) = \left(1+\frac{\Lambda^2}{\kappa^2}\right)^{-\Delta/2\nu} \tag{13}$$

To further simplify the kernel term, we are using an approximation in which $\kappa\left(\Delta\overline{T},\Delta\overline{\rho}\right)$ is defined as

$$\kappa^2\left(\Delta\overline{T},\Delta\overline{\rho}\right) = \frac{c_t}{a_o}\overline{\chi}^{-1}\left(\Delta\overline{T},\Delta\overline{\rho}\right) \tag{14}$$

where a_0 is a coefficient in the classical Landau expansion,[7,9] to be found from the slope of the dimensionless inverse susceptibility, $\overline{\chi}^{-1}\left(\Delta\overline{T},\Delta\overline{\rho}=0\right)=\overline{\rho}\left(\partial\overline{\rho}/\partial\overline{P}\right)_T$, along the critical isochore in the region unaffected by critical fluctuations. As a result of these simplifications, Eq. 12 becomes explicit in temperature and density, making the computations easier and avoiding the iterations needed in the complete crossover theory.

The crossover function $Y(\kappa)$, given by Eq. 13, modifies the behavior of the kernel term in such a way that asymptotically

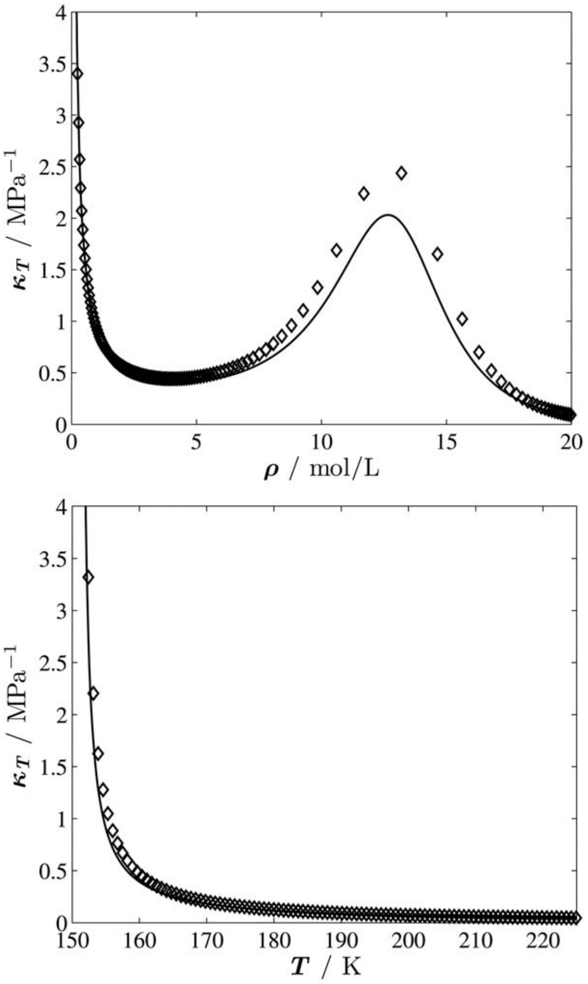

Figure 2. Top: Isothermal compressibility of argon as a function of density at $T = 153$ K. Bottom: Isothermal compressibility of argon as a function of temperature at the density $\rho = 13.40$ mol/L.

The symbols indicate values from the NIST database.[71] The curves represent values calculated from soft-SAFT.

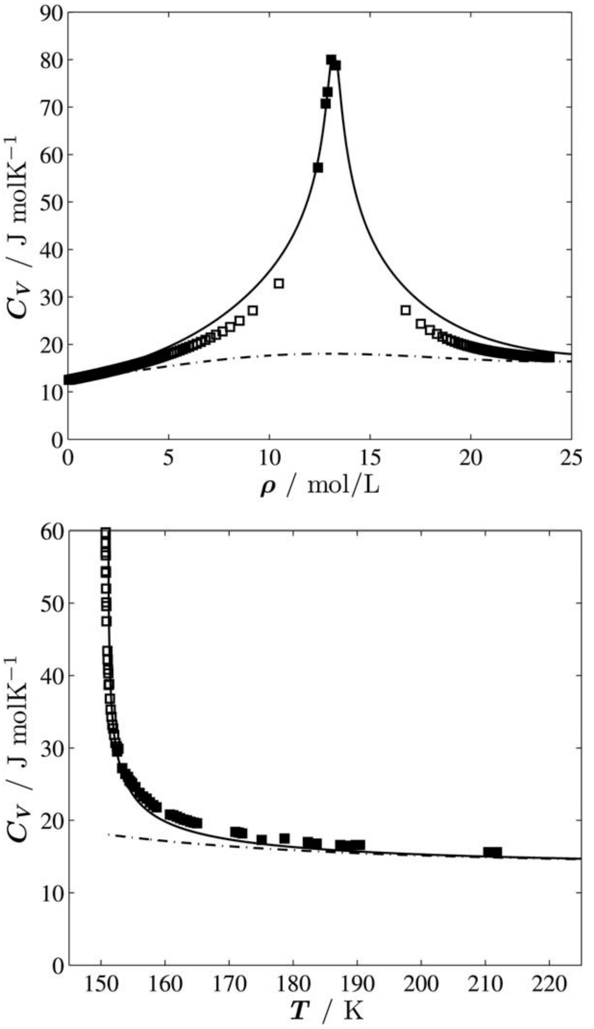

Figure 3. Top: Isochoric heat capacity of argon as a function of density at $T = 151.13$ K. Bottom: Isochoric heat capacity of argon as a function of temperature at $\rho = 13.292$ mol/L, which is the actual critical density according to accurate C_V measurements.

The solid curves represent values calculated from soft-SAFT including the kernel term. The dashes curves represent values calculated from soft-SAFT without the kernel term. In the top figure, open squares indicate values from the NIST database,[71] and filled squares indicate averaged experimental values of Anisimov et al.[69,70] In the bottom figure, open squares are data from Voronel et al.[68] and filled squares are data from Anisimov et al.[69]

close to the critical point, where the inverse distance κ^{-1} to the critical point and, hence, Λ^2/κ^2 diverges, the isochoric heat capacity $C_V=-T(\partial^2 A/\partial T^2)_V$ also diverges at the critical point. In particular, along the critical isochore, C_V asymptotically behaves as $C_V \propto \Delta\overline{T}^{-\alpha}$, with $\alpha=2-3\nu=0.11$. Away from the critical point, where $\Lambda^2/\kappa^2 \ll 1$, the kernel term vanishes and the isochoric heat capacity reduces to its classical (regular) behavior given by the mean-field equation of state.

Results

Soft-SAFT without kernel term

We tested soft-SAFT with and without the addition of the kernel term in Eq. 10 for argon. Argon was chosen because of the availability of very accurate experimental data for the isochoric heat capacity in the critical region.[68–70] Furthermore, the simplicity of the molecular interactions in argon enabled us to use a simple soft-SAFT molecular model.

We first applied soft-SAFT to argon without including the kernel term. Argon is a spherical molecule (the acentric factor is zero) and it is modeled as a homonuclear LJ sphere ($m = 1$) with a characteristic segment diameter σ and a dispersive energy ε (so the chain and association terms of soft-SAFT are set to zero). These LJ parameters were obtained from a fit to liquid density and vapor-pressure data from the National Institute of Standards and Technology database, from the triple point up to the critical point.[71] The constraint of matching the critical temperature ($T_c = 150.687$ K)[71] was initially included in the optimization algorithm. However, this restriction was leading to some inaccuracies in the representation of the isothermal compressibility in the critical region. Because an adequate representation of strongly divergent thermodynamic properties like the compressibility is a requisite for describing

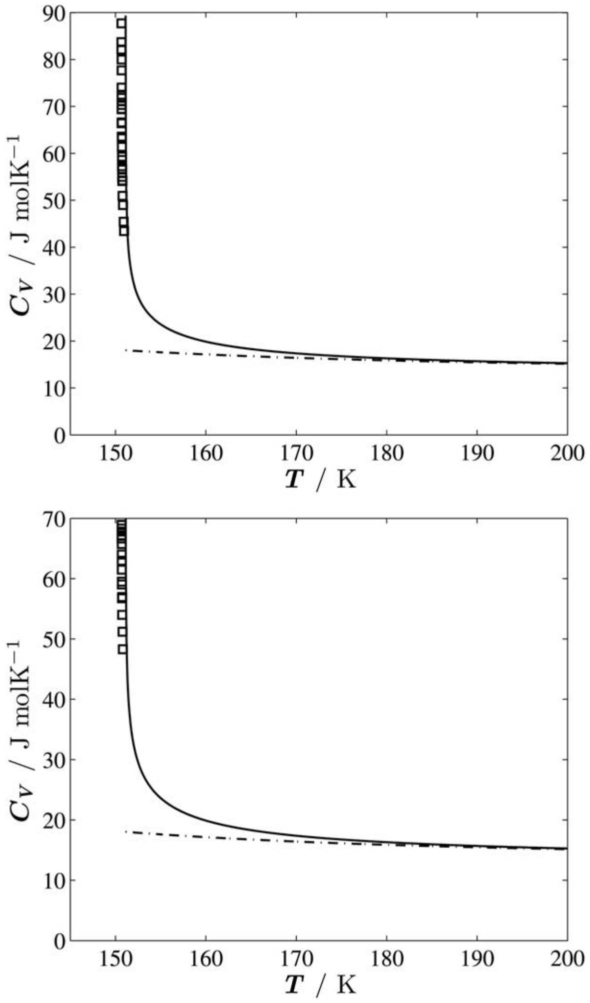

Figure 4. Top: Isochoric heat capacity of argon as a function of temperature at $\rho = 13.07$ mol/L. Bottom: Isochoric heat capacity of argon as a function of temperature at $\rho = 12.79$ mol/L.

The solid curves represent values calculated from soft-SAFT including the kernel term. The dashes curves represent values calculated from soft-SAFT without the kernel term. Symbols indicate experimental values of Anisimov et al.[69]

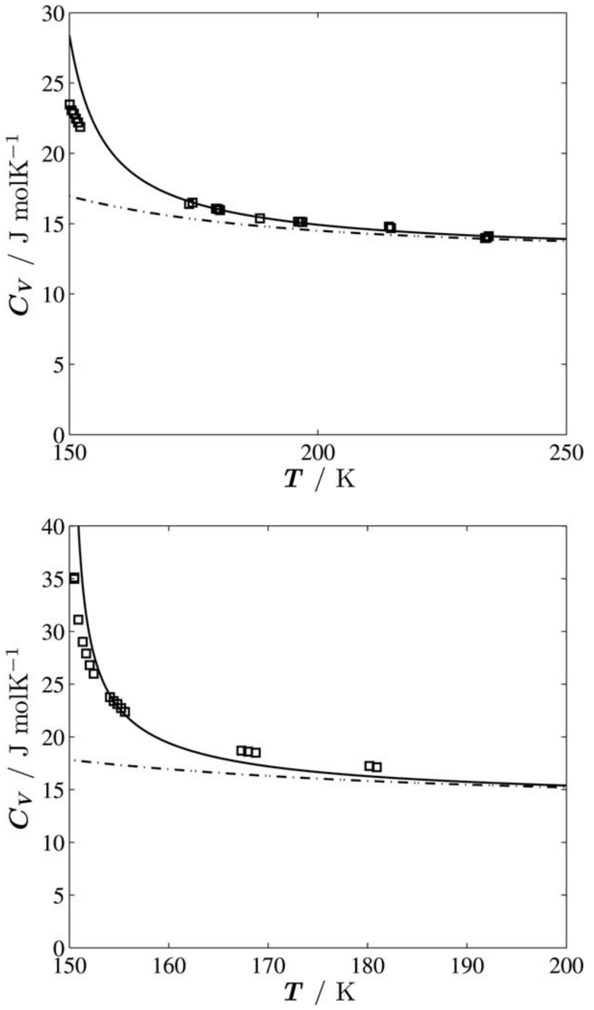

Figure 5. Top: Isochoric heat capacity of argon as a function of temperature at $\rho = 7.75$ mol/L. Bottom: Isochoric heat capacity of argon as a function of temperature at $\rho = 15.83$ mol/L.

The solid curves represent values calculated from soft-SAFT including the kernel term. The dashes curves represent values calculated from soft-SAFT without the kernel term. The symbols indicate experimental values experimental of Anisimov et al.[70]

weakly divergent thermodynamic properties through the addition of a kernel term, we made an attempt to improve the representation of the isothermal compressibility by removing the constraint of matching the critical temperature prior to the fit, obtaining $T_c = 151.125$ K, $\rho_c = 13.213$ mol/L, $P_c = 5.299$ MPa. The resulting optimized LJ parameters are

$$\sigma = 0.3388 \text{ nm}, \qquad \varepsilon/k_B = 115.12 \text{ K} \qquad (m=1) \tag{15}$$

The critical temperature is about 0.5 K above the actual critical temperature of argon, while the critical density is slightly lower from the actual critical density density ($\rho_c = 13.292$ mol/L) according to accurate C_V measurements.[68,69] This is no surprise, as mean-field equations always yield an apparent critical temperature that is overpredicted, affecting the rest of properties.[64] With this minor deviation of the critical temperature, the representation of the coexistence curve, of the saturation pressure, and of the density and temperature dependence of the isothermal compressibility in the critical region is shown in Figures 1 and 2.

Isochoric heat capacity

Having obtained a version of soft-SAFT that gives a reasonable representation of the isothermal compressibility, we now investigate whether a divergent isochoric heat capacity can be incorporated by including the contribution from the kernel term in Eq. 10 for the Helmholtz-energy density. The rescaling coefficient a_0 was deduced from the slope of the inverse susceptibility implied by the soft-SAFT equation. The rescaling coefficient c_t and the crossover parameter Λ were determined by comparing the formulation with the experimental data[68,69] for the isochoric heat capacity at constant near-critical density

$$a_0 = 2.73 \qquad c_t = 0.75 \qquad \Lambda = 0.40 \tag{16}$$

The isochoric heat capacity C_V of argon in the critical region is shown in Figures 3–5. The symbols indicate experimental data,[68–70] the solid curves represent values calculated from soft-SAFT with the contribution from the kernel term, and the dashed curves represent values calculated from soft-SAFT without the kernel term (original soft-SAFT). As can be inferred from these figures, soft-SAFT with the kernel contribution included gives a greatly improved representation of the divergent behavior of the isochoric specific heat. We believe that the remaining differences with the experimental data are caused by the fact that the multiparameter equation of state of the reference LJ fluid does already contain some limited enhancement effect. Finally, it is important to note that the original soft-SAFT parameters are not modified by the addition of the kernel term, as the inclusion of the treatment marginally affects the phase equilibrium properties other than the isochoric heat capacity.

Discussion

We have demonstrated that adding a kernel term, whose presence is predicted by the renormalization-group theory of critical phenomena, yields a significant improvement for the representation of the anomalous behavior of the isochoric heat capacity in the critical region. To obtain a more consistent representation of the isochoric heat capacity, we recommend the kernel term to be included in the multiparameter equation of state prior to determining the coefficients, including the rescaling parameter c_t and the crossover parameter Λ for the reference LJ fluid. For this purpose, additional computer simulation data for the reference LJ fluid near its critical point are desirable. As an alternative, one could select a monoatomic fluid, like argon, for which experimental data in the critical region are available, as the reference fluid in applying soft-SAFT to other fluids. In this case, the reference fluid will already contain a diverging isochoric heat capacity, so that adding a kernel term a posteriori will no longer be needed.

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