

CROSSOVER SAFT-BACK EQUATION OF STATE FOR CO₂ AND H₂O

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Abstract The crossover statistical associating fluid theory and Boublik-Alder-Chen- Kreglewski (SAFT-BACK) equation of state (EOS) is established. The system-dependent parameters for CO₂ and H₂O are regressed and their thermodynamic properties are calculated. Then the classical and crossover SAFT-BACK EOSs are compared. For CO₂, their calculated deviations are both small. For H₂O, the calculated accuracy with the crossover EOS is better than that with the classical EOS.

Introduction

Because the classical EOSs and the critical theories are complementary, many efforts have been made to construct a kind of molecular thermodynamic model, which integrates the critical theories into a classical EOS, to accomplish the crossover of the critical region and the uncritical region. In this work, the crossover SAFT-BACK EOS is proposed and is used to calculate the thermodynamic properties for CO₂ and H₂O.

I Nonclassical Helmholtz free energy of a crossover EOS

In terms of the crossover method by Kiselev [1], the dimensionless molar Helmholtz free energy for a crossover EOS can be written as

$$\bar{A}(T, v) = \Delta \bar{A}(\bar{t}, \Delta \bar{h}) - \Delta v \bar{P}_0(T) + \bar{A}_0^{\text{res}}(T) + \bar{A}_0(T) - \ln v_{0c} - k(\bar{t}^2) \quad (1)$$

where

$$\Delta \bar{A}(\bar{t}, \Delta \bar{h}) = \bar{A}^{\text{res}}(\bar{t}, \Delta \bar{h}) - \bar{A}^{\text{res}}(\bar{t}, 0) - \ln(\Delta \bar{h} + 1) + \Delta \bar{h} \bar{P}_0(\bar{t}, 0) \quad (2)$$

$$\bar{P}_0(T) = P(T, v_{0c}) v_{0c} / RT \quad (3)$$

$$\bar{A}_0^{\text{res}}(T) = a^{\text{res}}(T, v_{0c}) / RT \quad (4)$$

$$k(\bar{t}^2) = \frac{1}{2} a_{20} \bar{t}^2 (Y^{-a/\Delta_1} - 1) + \frac{1}{2} a_{21} \bar{t}^2 (Y^{-(a-\Delta_1)/\Delta_1} - 1) \quad (5)$$

and $\bar{A}_0(T)$ is only related to the temperature and is not used in the calculation.

In Eq.(2), \bar{t} and $\Delta \bar{h}$ are the renormalized temperature and the order parameter respectively

$$\bar{t} = t Y^{-a/2} + (1+t) \Delta t_c Y^{2(2-a)/3} \quad (6)$$

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$$\Delta\bar{\mathbf{h}} = \Delta\mathbf{h}Y^{(g-2\mathbf{b})/4?_1} + (1 + \Delta\mathbf{h})\Delta\mathbf{h}_c Y^{2(2-a)/2?_1} \quad (7)$$

In above equations

$$\mathbf{t} = T/T_c - 1, \quad \Delta\mathbf{h} = v/v_c - 1 \quad (8)$$

$$\Delta\mathbf{t}_c = T_c/T_{0c} - 1, \Delta\mathbf{h}_c = v_c/v_{0c} - 1 \quad (9)$$

where T_c and v_c are the real critical parameters; T_{0c} and v_{0c} are the classical critical ones that can be found through the conditions

$$P_{0c} = -\left(\frac{\partial A}{\partial v}\right)_{T_{0c}}, \quad \left(\frac{\partial^2 A}{\partial v^2}\right)_{T_{0c}} = 0, \quad \left(\frac{\partial^3 A}{\partial v^3}\right)_{T_{0c}} = 0 \quad (10)$$

In earlier equations, Y is the crossover function and can be written in the parametric form

$$Y(q) = \left(\frac{q}{1+q}\right)^{2\Delta_1} \quad (11)$$

where q is the parametric variable and can be found from the solution of the equation [2]

$$\left(q^2 - \frac{\mathbf{t}}{Gi}\right) \left[1 - \frac{p^2}{4b^2} \left(1 - \frac{\mathbf{t}}{q^2 Gi}\right)\right] = \frac{b^2}{Gi^{2b}} \left(\frac{q}{1+q}\right)^{2(1-2b)} \times \left\{\Delta\mathbf{h}\left[1 + v_1\Delta\mathbf{h}^2 \exp(-d_1\Delta\mathbf{h})\right] + d_1\mathbf{t}(1-2\mathbf{t})\right\}^2 \quad (12)$$

where $p^2 = b^2 = 1.359$ and $d_1 = 8.5$ [2].

In above equations, $\mathbf{g} = 1.24$, $\mathbf{b} = 0.325$, $\mathbf{a} = 2 - \mathbf{g} - 2\mathbf{b} = 0.110$ and $\Delta_1 = 0.51$ are the current best estimates of the nonclassical critical exponents [3].

The pressure equation for the crossover EOS is

$$P(T, v) = -\left(\frac{\partial A}{\partial v}\right)_T = \frac{RT}{v_{0c}} \left[-\frac{v_{0c}}{v_c} \left(\frac{\partial \Delta\bar{A}(\bar{\mathbf{t}}, \Delta\bar{\mathbf{h}})}{\partial \Delta\bar{\mathbf{h}}}\right)_T + \bar{P}_0(T) + \frac{v_{0c}}{v_c} \left(\frac{\partial k}{\partial \Delta\bar{\mathbf{h}}}\right)_T \right] \quad (13)$$

In conclusion, five thermodynamic functions, $\bar{P}_0(T)$, $\bar{A}_0^{\text{res}}(T)$, $\bar{A}^{\text{res}}(\bar{\mathbf{t}}, \Delta\bar{\mathbf{h}})$, $\bar{A}^{\text{res}}(\bar{\mathbf{t}}, 0)$ and $\bar{P}_0(\bar{\mathbf{t}}, 0)$, are required in the process of the transformation of a classical EOS into the crossover form. Their detailed formulas are determined by the form of a classical EOS.

A crossover EOS contains five new system-dependent parameters, Gi , d_1 , v_1 , a_{20} and a_{21} . Gi is the Ginzburg number for the fluid of interest [4].

II Crossover SAFT-BACK EOS

Zhang et al. [5] modified the BACK EOS with the associating term of the SAFT EOS and proposed the SAFT-BACK EOS. The new EOS can be extended to associating fluids. Based on their work, we deduced the crossover SAFT-BACK EOS.

In SAFT-BACK EOS, u^0 , v^{00} , \mathbf{a}_0 , e/k , \mathbf{k}^{AB} and \mathbf{e}^{AB} are the system-dependent parameters, D_{ij} is the universal constants, $C = 0.12$ and $\mathbf{h}_0 = \sqrt{2}\mathbf{p}/6$ [5].

Five thermodynamic functions for the crossover EOS are obtained by replacing original variables T and v in the function \bar{A}^{res} and Z with new ones. These functions are given by

$$\bar{P}_0(T) = Z(T, v_{0c}) \quad (14)$$

$$\bar{A}_0^{\text{res}}(T) = \bar{A}(T, v_{0c}) \quad (15)$$

$$\bar{A}^{\text{res}}(\bar{t}, \Delta\bar{h}) = \bar{A}(T_{0c}(\bar{t} + 1), v_{0c}(\Delta\bar{h} + 1)) \quad (16)$$

$$\bar{A}^{\text{res}}(\bar{t}, 0) = \bar{A}(T_{0c}(\bar{t} + 1), v_{0c}) \quad (17)$$

$$\bar{P}_0(\bar{t}, 0) = Z(T_{0c}(\bar{t} + 1), v_{0c}) \quad (18)$$

III Fitting the parameters of fluids for the SAFT-BACK EOS

In the crossover SAFT-BACK EOS, $k(\bar{t}^2)$ is the kernel term that can express the caloric properties [6]. In order to simplify our computation, we limited our calculation only on the $P?T$ and vapor-liquid equilibria (VLE) properties but not on the caloric properties. Therefore, we set both a_{20} and a_{21} as zero. So the crossover SAFT EOS contains three sets of system-dependent parameters: (1) the SAFT-BACK parameters, u^0 , v^{00} , \mathbf{a}_0 , e/k , \mathbf{k}^{AB} and \mathbf{e}^{AB} , (2) the crossover parameters, Gi , d_1 and v_1 , (3) the real critical parameters of fluids, T_c and v_c .

We selected two typical pure fluids, CO_2 and H_2O . Because v_1 affects the thermodynamic properties of fluids very little, we set it as its order of magnitude and $v_1 = 0.001$. The values of T_c and v_c equal to their experimental ones, shown in Table 1. For CO_2 , $\mathbf{e}^{\text{AB}} = \mathbf{k}^{\text{AB}} = 0$ and $e/k = 52$ [5], and so it contains five adjustable parameters, u^0 , v^{00} , \mathbf{a}_0 , Gi and d_1 . For H_2O , $e/k = 10$ [7], and consequently it contains seven adjustable parameters, u^0 , v^{00} , \mathbf{a}_0 , \mathbf{k}^{AB} , \mathbf{e}^{AB} , Gi and d_1 . We adopted the association scheme of 3B for water [7, 8, 9]. We find these parameters for two pure fluids by fitting the crossover SAFT-BACK EOS to their experimental saturated vapor pressure and liquid density data. In this work, all experimental data are from [10]. The values of all system-dependent parameters for these fluids in the crossover SAFT-BACK EOS are listed in Table 2.

IV Comparison with the experimental VLE and $P?T$ data and discussion

The calculated deviations of the VLE and $P?T$ properties for CO_2 and H_2O with the crossover SAFT-BACK and classical SAFT-BACK EOS are listed in Table 3. And their results are shown in Figs. 1-6. For CO_2 , a nonassociating fluid, the calculated deviations with two EOSs are both very small. For H_2O , an associating fluid, the calculated deviations with the crossover EOS are far smaller than those with the classical EOS.

The size of the critical region of one fluid measured in terms of $|\bar{t}|$ is approximately proportional to its Ginzburg number. For CO_2 , the Ginzburg number in the crossover SAFT-BACK EOS is very small ($Gi \approx 0.01$) and, consequently, its critical region is very small too. In this work, the experimental data of CO_2 are far from its critical region, and so the calculated accuracy with the classical EOS is almost as good as that with the crossover one. For H_2O , the Ginzburg number is rather large ($Gi \approx 0.1$) and, consequently, the critical

region is also rather large. The accuracy with the crossover EOS is much better than that with the classical one. Based on above analysis, we can classify most of fluids into two types. For some fluids, such as CO₂, methane, ethane, propane and ethane etc., their Ginzburg numbers in some classical EOSs, for example the SAFT-BACK EOS and the Benedict-Webb-Rubin (BWR) EOS [11], are very small. Therefore, these EOSs have good accuracy in the whole range of experimental data and the crossover method will not give a visual improvement. However, it is expected that the crossover method can give better results than the classical one when more narrow temperature region is considered. For other fluids, such as H₂O and ammonia etc., their Ginzburg numbers for most of EOSs are very large. Accordingly, their critical regions are very large and the crossover method gives a great visual improvement in the wide range near the critical point.

Consequently, the Ginzburg number is one criterion through which the valid application range of a classical EOS can be roughly estimated. Its order of magnitude is 10⁻¹-10⁻². The size of the Ginzburg number for one fluid depends on its kind and its molecular weight. Gi is proportional to $(\bar{l}/l_0)^6$, where \bar{l} is an average distance between particles and l_0 is an average interaction range (effective size) of the molecule. Therefore, in ionic systems with the long-range interaction, the Ginzburg number is smaller than that in simple fluids [12]. It is also expected that the Ginzburg number decreases as the molecular weight increases in polymer and associating fluids [2,6,13]. However, in [9], a good description of experimental data for n-alkanes was achieved with the increasing values of the Ginzburg number. In binary polymer blends the Ginzburg number was also found much larger than that in simple binary mixtures [14]. So the question how does the Ginzburg number in fluids depend on the molecular weight is still remaining open.

Conclusion

The application of the crossover method should be combined with a classical EOS. Some EOSs, such as the SAFT EOS, the crossover method is better than the classical one for most of fluids. Other EOSs, such as the SAFT-BACK EOS, the crossover method is not necessarily adopted in industrial calculation for some simple fluids and only for associating fluids the crossover method can give a marked improvement.

Acknowledgment

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Table1 Experimental values of the critical parameters for CO₂ and H₂O

	T_c^{exp} (K)	r_c^{exp} (mol/l)	P_c^{exp} (MPa)
CO ₂	304.13	17.874	7.3773
H ₂ O	647.10	10.625	22.064

Table2 Parameters for CO₂ and H₂O for the crossover SAFT-BACK EOS

	u^0/k (10 ² K)	v^{00} (ml/mol)	a_0	e^{AB}/k (10 ³ K)	k^{AB} (10 ⁻²)	e/k	G_i (10 ⁻²)	d_1	v_1 (10 ⁻³)
CO ₂	2.6184	21.347	1.0042	0	0	52	1.0212	1.5000	1.000
H ₂ O	5.8633	9.0098	1.7999	2.4699	6.1001	10	9.6000	2.5000	1.000

Table 3 Calculated deviations for VLE and P ? T properties

VLE				P ? T			
T range (K)	AAD% of P^{sat}		AAD% of ?		T range (K)	AAD% of P	
	CLSB	CRSB	CLSB	CRSB		CLSB	CRSB
H ₂ O 503.15-646.90	1.8351	0.52320	21.459	3.3710		7.5287	1.8379
CO ₂ 220.00-304.00	0.23296	1.1790	1.6488	1.8439	285-360	1.7416	1.5977

(note: CLSB=Classical SAFT-BACK EOS; CRSB=Crossover SAFT-BACK EOS)

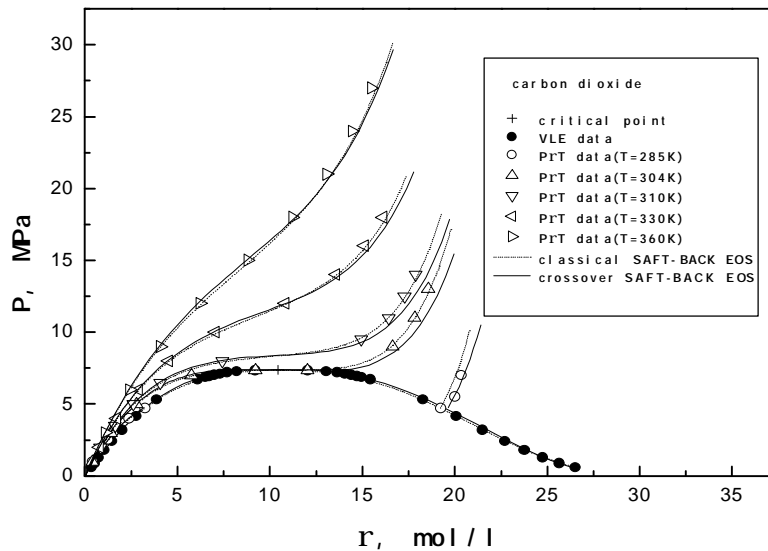


Figure 1 P - r diagram for CO₂

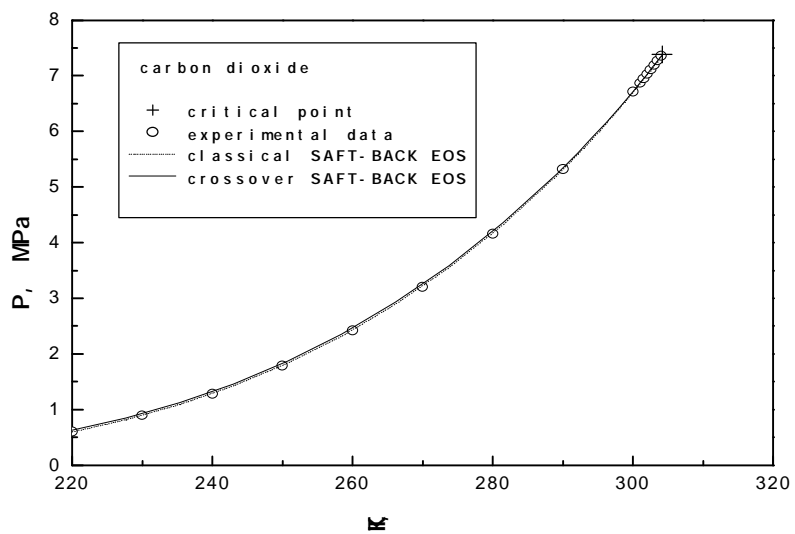


Figure 2 Saturated pressures for CO₂

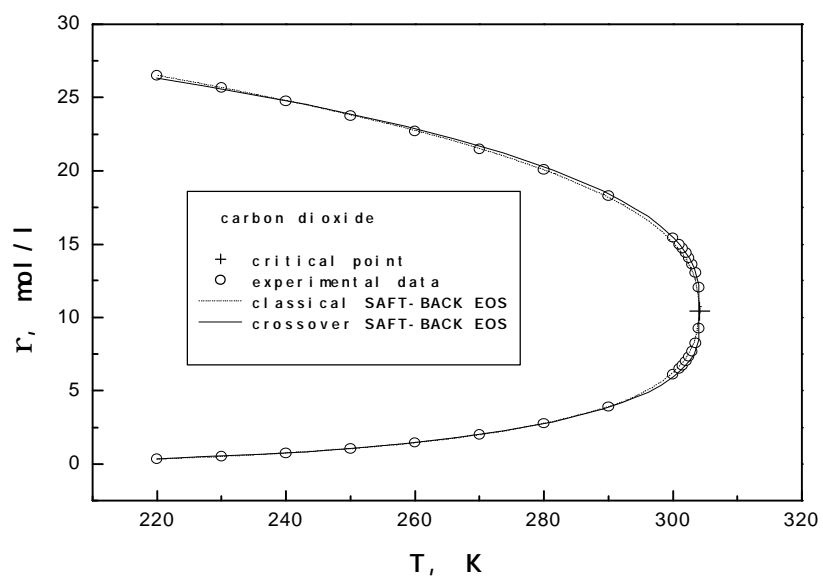


Figure 3 Saturated densities for CO₂

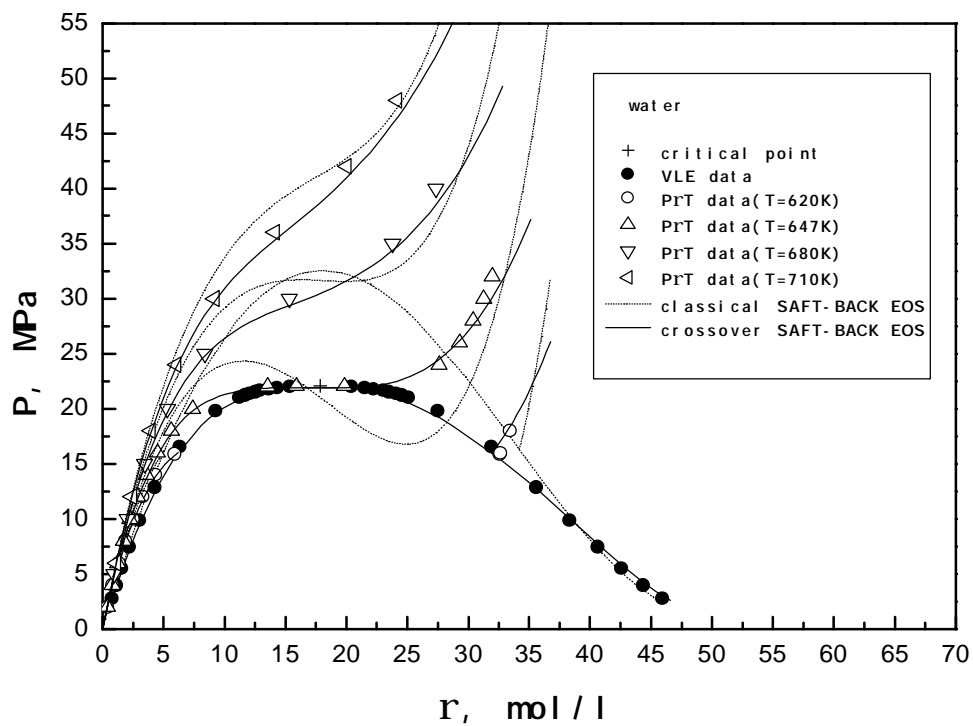


Figure 4 P - γ diagram for H_2O

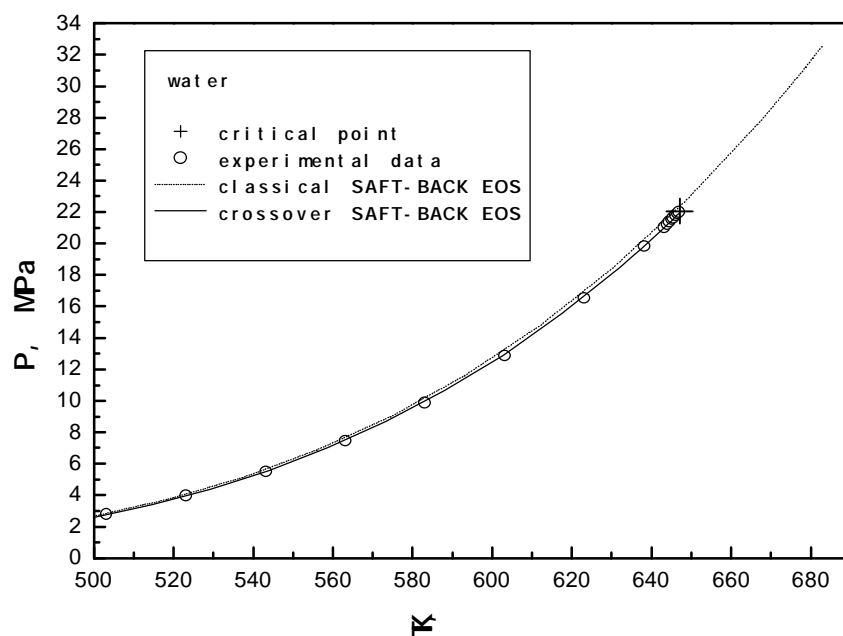


Figure 5 Saturated pressures for H_2O

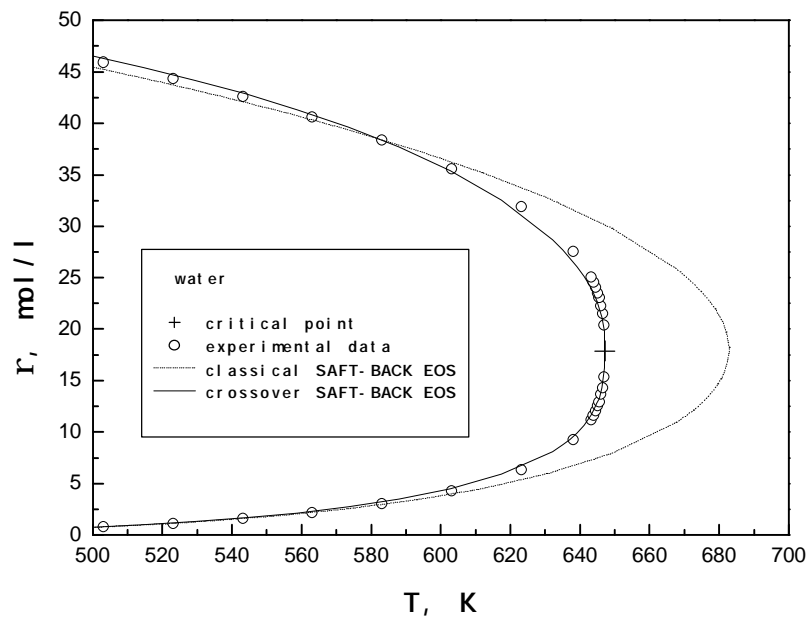


Figure 6 Saturated densities for H₂O