임계영역부터 이상기체 영역까지에 대한 크로스오버 삼차 상태방정식

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A Crossover Cubic Equation of State Near to and Far from the Critical region

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Introduction

The classical cubic equations of state fail to reproduce the non-analytical, singular behavior of fluids in the critical region by long-scale fluctuations in density. Supercritical fluids are characterized by large inhomogeneity of molecular distribution. The density fluctuation is a suitable parameter for quantitative and direct description of the inhomogeneity from the view of mesoscopic or microscopic scale. In this research, we use the Patel-Teja(PT) cubic equation of state with a new alpha function and develop a crossover cubic model using the sine model near to and far from the critical region which incorporates the scaling laws asymptotically close to the critical point and its transformed into the classical cubic equations of state far away from the critical point. We show that, over a wide range of states, the crossover cubic equation of state yields a much better representation of the thermodynamic properties of supercritical fluids than the classical Patel-Teja equations of state.

Theory

In the present work we apply the crossover theory to the PT equation of state. The PT equation of state has the form

$$P=\frac{RT}{V-b}-\frac{a}{V(V+b)+c(V-b)} \tag{1}$$

$$a=\Omega_a\frac{R^2T_c^2}{P_c}a_0(T),\ b=\Omega_b\frac{RT_c}{P_c},\ c=\Omega_c\frac{RT_c}{P_c}$$

$$\Omega_c=1-3Z_c$$

$$\Omega_a=3Z_c^2+3(1-2Z_c)\Omega_b+\Omega_b^2+\Omega_c$$

and where Ω_b is the smallest positive root of the following equation.

$$\Omega_b^3+(2-3Z_c)\Omega_b^2+3Z_c^2\Omega_b-Z_c^3=0$$

But we chose a form proposed by Stryjek, R. and Vera, J.H. for $a_0(T)$ term to reduce the number of parameters.

$$a_o(T) = [1 + \varkappa(1 - T_R^{0.5})]^2$$

$$\varkappa = \varkappa_0 + \varkappa_1(1 + T_R^{0.5})(0.7 - T_R)$$

$$\varkappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3$$

By the transformation of a classical expression for the Helmholtz free energy into the crossover form, we obtain the crossover cubic equation of state(New Xcubic EOS).

$$P(T,V) = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{RT}{V}\left[-\frac{V_{oc}}{V_c}\left(\frac{\partial \Delta \overline{A}}{\partial \Delta\eta}\right)_T + \overline{P}_o(T) + \frac{V_{oc}}{V_c}\left(\frac{\partial K}{\partial \Delta\eta}\right)_T\right] \quad (2)$$

$$\overline{A}(T,V) = \Delta\overline{A}(\overline{\tau}, \overline{\Delta\eta}) - \frac{V}{V_{oc}}\overline{P}_0(T) + \overline{\mu}_0(T) \quad (3)$$

where,

$$\overline{P}_o(T) = \frac{1}{b_1} - \frac{T_{oc}}{T}\frac{\Omega_a a_0(T)}{Z_{oc} b_2 b_3}$$

$$\Delta\overline{A}(\overline{\tau}, \overline{\Delta\eta}) = -\ln\left(\frac{\Delta\eta}{b_1} + 1\right) + \frac{T_{oc}}{T}\frac{\Omega_a a_o(\overline{\tau})}{\Omega}\ln\left(\frac{\Delta\eta / b_2 + 1}{\Delta\eta / b_3 + 1}\right) + \frac{\Delta\eta}{b_1} - \frac{T_{oc}}{T}\frac{\Omega_a a_0(\overline{\tau})\Delta\eta}{Z_{oc} b_2 b_3}$$

and the renormalized values is given by

$$\overline{\tau} = \tau Y^{-\frac{\alpha}{2\Delta_1}}, \quad \overline{\Delta\eta} = \Delta\eta Y^{\frac{(\gamma - 2\beta)}{4\Delta_1}} + (1 + \Delta\eta)\Delta\eta_c Y^{\frac{(2-\alpha)}{2\Delta_1}}$$

and the crossover function Y can be written in following form obtained by Kiselev et al.

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

In this research, we find q from a solution of the crossover sine model(SM)

$$\left(q^2 - \frac{\tau}{Gi}\right)\left[1 - \frac{p^2}{4b^2}\left(1 - \frac{\tau}{q^2 Gi}\right)\right] = b^2 \frac{\Delta\eta[1 + v_1\exp(-10\Delta\eta)] + d_1\tau^2}{m_0 Gi^\beta} Y^{\frac{(1-2\beta)}{\Delta_1}}$$

where, $v_1, d_1, m_0,$ and Gi are the system-dependent parameters, while the universal parameters b^2 and p^2 are set equal to the linear model parameter.

Comparison with experimental data for pure fluids

The New Xcubic EOS contains five classical system-dependent parameters : $P_{oc}, T_{oc}, Z_{oc}, \omega$ and $\varkappa_1$. In addition to the classical parameters, this EOS also contains the Grinzburg number Gi, the critical shift Δv_c, the coefficients v_1, d_1, m_0.

Thus this EOS contains 10 adjustable parameters.

But, ω is already known and parameter m_0 is not sensitive to the choice of fluid.(m_0=1.)

Also, using the conditions $T_{oc} = T_c$ and $P_{oc} = P_c$, one can reduce the number of adjustable parameters to five.

In this work, we tested the New Xcubic EOS against experimental data for Carbon dioxide, and from methane to heptane. Z_{oc}, Gi, $\varkappa_1$, v_1, d_1 were found from a fit of (2) to experimental VLE- and PVT-data in one and two-phase regions.

The system-dependent parameters are listed in Table 1.

Table 1. System-dependent parameters for the New Xcubic EOS

Components	Classical parameters					Critical shift	Crossover parameters		
	$T_{\alpha c}$ (K)	$P_{\alpha c}$ (bar)	$Z_{\alpha c}$	χ_1	ω	Δv_c	Gi	v_1	d_1
CO_2	304.128	73.773	0.327426	-0.23213	0.22394	-0.16133	0.052759	0.010199	1.9647
CH_4	190.564	45.992	0.332694	-0.11693	0.01142	-0.13942	0.11248	0.02854	-2.04011
C_2H_6	305.33	48.718	0.332675	-0.3361	0.0993	-0.16028	0.107135	0.016761	1.75295
C_3H_8	369.85	42.4766	0.329581	-0.20188	0.15243	-0.16173	0.06637	0.01665	-1.53766
C_4H_{10}	425.16	37.96	0.327444	-0.38834	0.19958	-0.16336	0.13136	0.017574	2.51526
C_5H_{12}	469.7	33.665	0.324339	-0.3091	0.251	-0.17342	0.0692	0.01502	-0.50559
C_6H_{14}	507.82	30.181	0.323641	-0.34773	0.297	-0.18372	0.136737	0.014138	1.959101
C_7H_{16}	540.13	27.27	0.318534	-0.0841	0.348	-0.17659	0.08899	0.01186	-0.1041

And comparisons of the predictions of the model with experimental data are shown in Figs. 1-2.

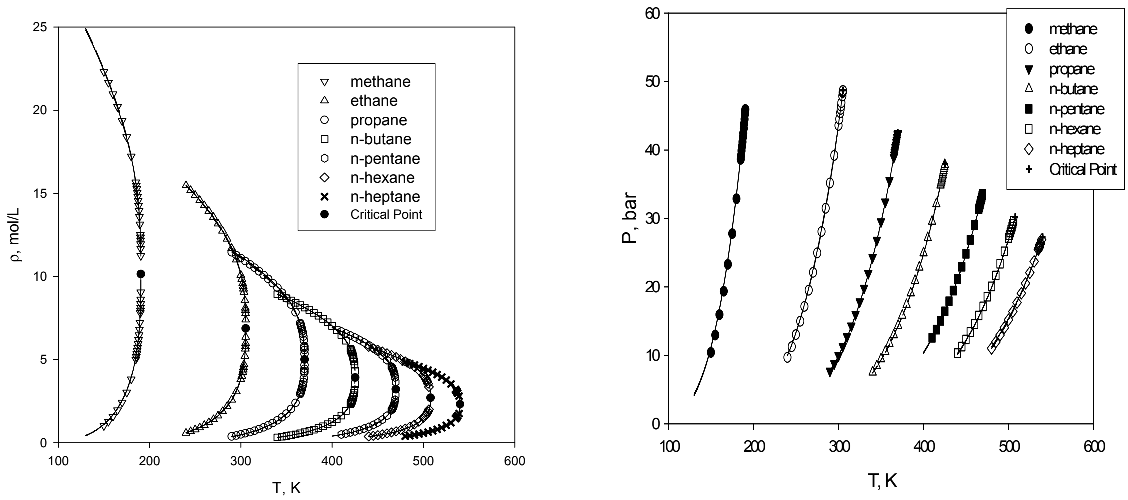

Fig 1. The saturated density(left) and vapor pressure(right) data for Hydrocarbons which are from methane to heptane with prediction of the New Xcubic EOS(solid curves) and XPT EOS(dashed curves)

The deviations of the VLE properties calculated with the New Xcubic EOS, XPT EOS, and PT EOS are listed in Table 2.

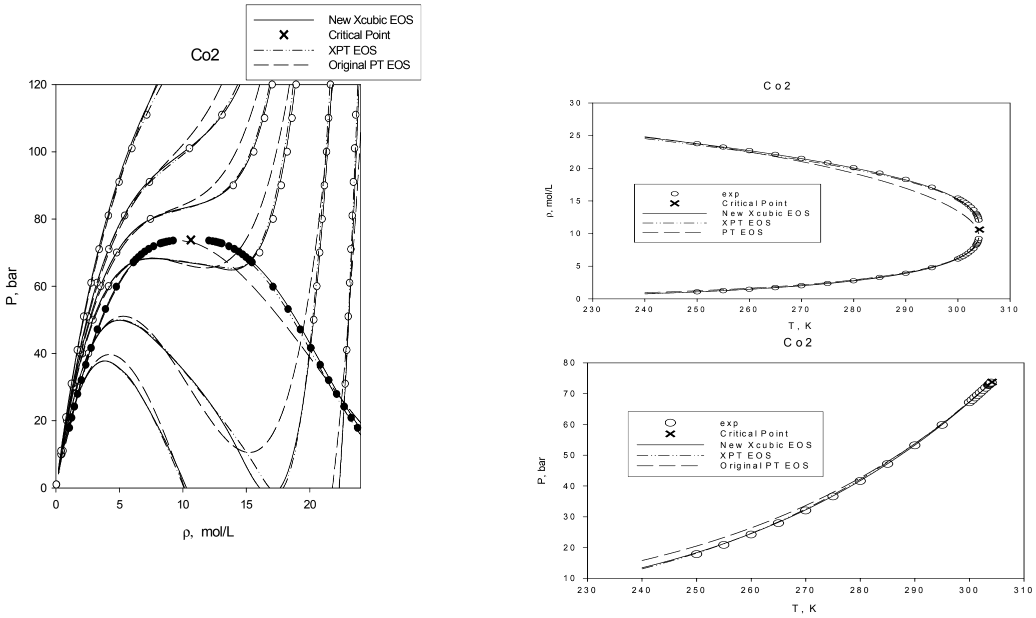

Fig 2. $P\rho T$ data(left) and VLE data(right) for Carbon dioxide with predictions of the New Xcubic EOS, the XPT EOS and PT EOS

Table 2. Calculated deviations for VLE properties

components	$AADP(\%)$			$AAD\rho(\%)$ saturated vapor			$AAD\rho(\%)$ saturated liquid			T range, K
	New Xcubic EOS	XPT EOS	PT EOS	New Xcubic EOS	XPT EOS	PT EOS	New Xcubic EOS	XPT EOS	PT EOS	
CO_2	0.4434	0.7312	2.4439	1.238	1.6563	4.5769	0.9555	1.59678	9.704	240~304
CH_4	1.7213	1.8504	3.9462	3.8527	3.8813	7.3053	0.1902	1.08313	9.0275	150~190
C_2H_6	0.87794	1.0808	2.0265	2.03259	2.1159	4.434	0.87794	0.7729	8.4582	240~305
C_3H_8	0.2481	0.7386	2.0179	1.4818	2.2449	4.5053	0.94772	0.6092	8.4669	290~369
C_4H_{10}	0.4297	0.4884	2.2802	0.8997	1.5974	4.147	0.1249	0.2139	6.2768	340~425
C_5H_{12}	0.1551	0.1388	1.88264	1.03015	0.93704	4.1239	1.1234	0.3772	9.7067	400~469
C_6H_{14}	0.8982	0.9591	4.55575	2.24859	2.5662	8.4636	2.514	2.6087	8.45611	440~507
C_7H_{16}	0.6594	0.1796	4.82821	1.2608	2.7471	10.0969	1.1485	2.6965	8.5473	480~540

Conclusions

The New Xcubic EOS successfully can describe the VLE and $P\rho T$ data over a wide range and the deviations are very small.

References

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