A new crossover sine model based on trigonometric model and its application to the Crossover Lattice equation of state

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Ⅰ. INTRODUCTION

In this paper we present the development of a new sine model (NSM) which has theoretical strictness compared with previous model and apply this new model to calculations of thermodynamics properties and phase behaviours of pure fluids and fluid mixtures. We start by reviewing the crossover theory developed by Kiselev and describing the crossover lattice EOS. And then, the CSM is discussed and we present the process of developing a NSM, followed by a comparison of our new model with the previous one, and then describe in detail the characteristic features of the NSM. Finally, we discuss the implementation of the crossover lattice EOS using the NSM for various pure fluids and fluid mixtures, as a demonstration of a successful application of this new model to a crossover EOS.

II. THE NEW CROSSOVER SINE MODEL

we obtained the new sine model (NSM) and crossover function.

$$(M + d_1\tau)^2 \frac{p^2}{m_0^2 r^{2\beta}} q_1^{2-4\beta} = \frac{3}{4} q_1^2 - \frac{\tau}{2Gi} - \frac{\tau^2}{4Gi^2 q_1^2} \tag{1}$$

$$Y(q) = \left(\frac{q}{1+q}\right)^{2\Delta_1} \qquad \text{where } q = q_1 e^{0.1\varphi}. \tag{2}$$

Near the critical point, φ goes to zero and then q becomes equal with q_1, which incorporates the scaling laws. Far from the critical point, φ goes to infinity and the xLF EOS is then reduced to the original EOS.

III. COMPARISON WITH THE CROSSOVER SINE MODEL

The NSM has the following characteristic features compared to the CSM. First, in developing the CSM, the parametric variable *M* was substituted with variable φ and $R(q)^{-\beta+\frac{1}{2}}$ was also introduced:

$$\varphi = m_0 r^\beta R(q)^{-\beta+\frac{1}{2}} \sin(q\theta)/q + d_1\tau \tag{3}$$

where $R(q) = q^2 / Y(q)^{1/\Delta_1}$. And combining the two parametric variables, one obtained:

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

In this equation, the *q* value shows symmetric behavior around the critical density at an isotherm and, thus, for introducing the asymmetry of the *q* value, φ was replaced with the empirical expression $\varphi[1 + v_1 \exp(-10\varphi)]$ and, in this procedure, the additional crossover parameter v_1 was used.

However, here we derived the NSM with the original parametric variables M and τ, as the NSM itself has asymmetry of the q value around the critical point, as shown in its expression and we thus did not need any additional empirical expressions.

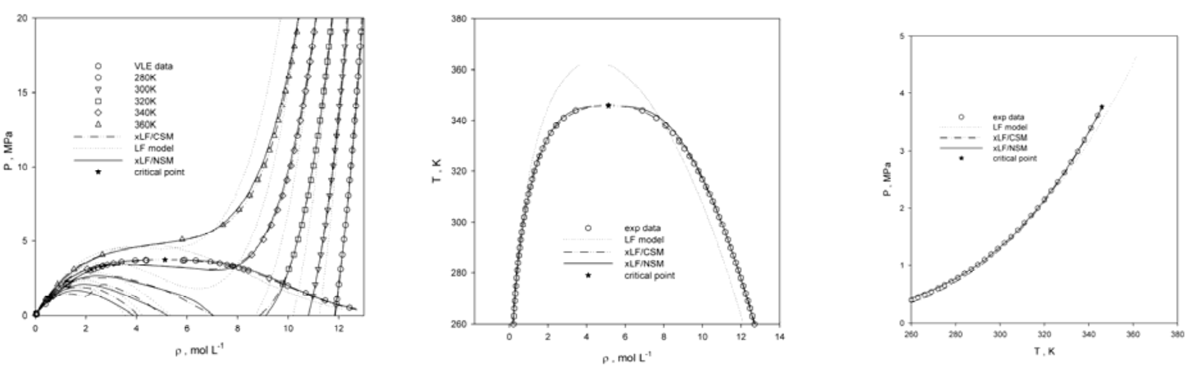
$$(M + d_1\tau)^2 \frac{p^2}{m_0^2 r^{2\beta}} q_1^{2-4\beta} = \frac{3}{4} q_1^2 - \frac{\tau}{2Gi} - \frac{\tau^2}{4Gi^2 q_1^2} \tag{5}$$

Setting d_1 as an adjustable parameter caused no significant improvements in representing phase behavior of pure fluids. Thus, in this work, we used d_1 as a universal parameter (-1).

Ⅳ. RESULTS AND DISCUSSION

A. Application to pure systems

FIGURE 1. $P\rho T$ data and VLE data (Ref. 24) for R143a with correlations of the xLF/NSM (solid curves), the xLF/CSM (dashed-dot-dot curves) and LF model (dotted curves).



B. Application to mixture systems

FIGURE 2. Vapor-liquid equilibria (Ref. 28) of the CO_2 (1)/R124(2) system with predictions of the xLF/NSM (solid curves), the xLF/CSM (dash-dot-dot curves) and the LF EOS(dotted curves).

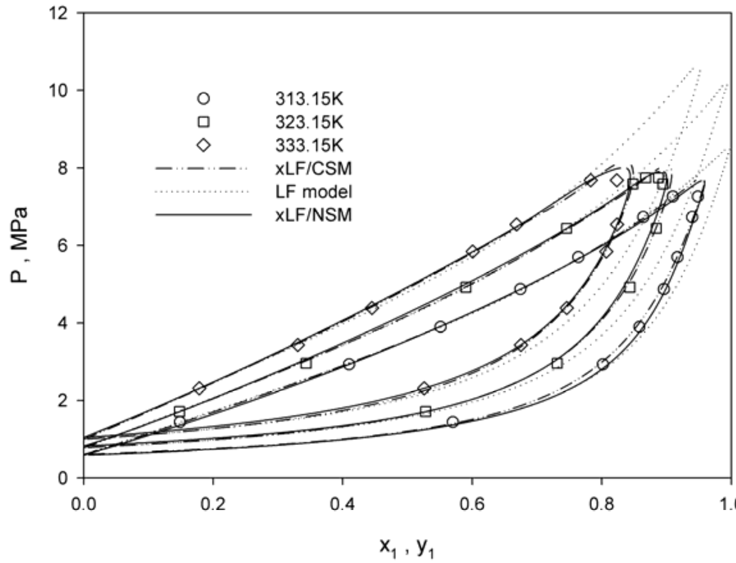
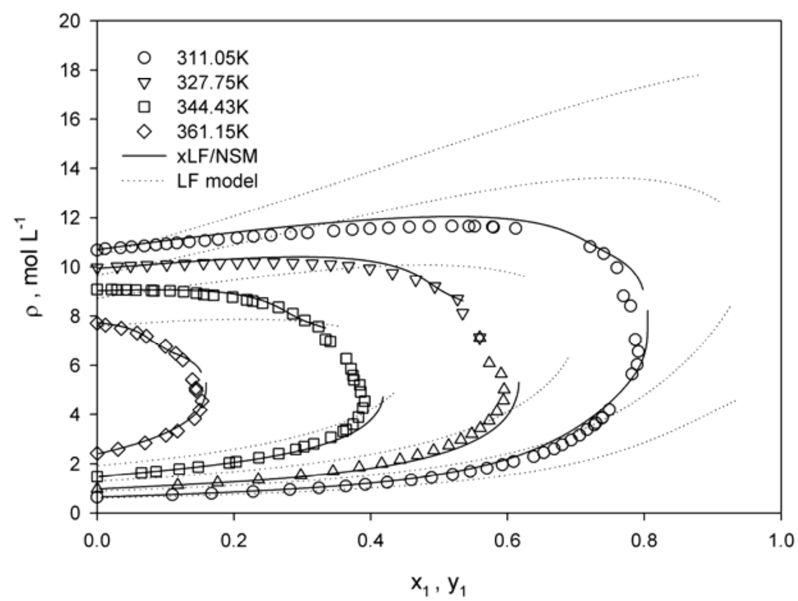


FIGURE 3. Vapor-liquid equilibria (Ref. 32) of the CO_2/propane system with predictions of the xLF/NSM (solid curves) and the LF EOS(dotted curves).



V. CONCLUSIONS

In this paper, we developed a new crossover sine model (NSM) and applied this model to the crossover lattice equation of state for calculation of thermodynamic properties and phase behaviors of various fluid systems. Our new model has several improved features compared with the crossover sine model (CSM). The CSM model used previously needed an additional empirical expression to satisfy the asymmetry condition of q value and this term had an additional crossover parameter. However, NSM model contents the asymmetry condition without any additional empirical expression and additional crossover parameter, because it was developed with keeping a theoretical base of the parametric model. Also this theoretical strictness enables d_1 used as a constant value and the crossover equation of state using the NSM has only one additional crossover parameter besides original parameters. To demonstrate the performance of the NSM model, we calculated phase behaviors of pure fluids and fluid mixtures using the xLF/NSM model. For both pure and mixture systems, the xLF/NSM model correlated phase behaviors well in a wide range including critical and supercritical region than the LF model. And the xLF/NSM model showed calculation results comparable to the xLF/CSM model, though the xLF/NSM has fewer system-dependent parameters.

The xLF/NSM model showed accurate correlations for thermodynamic properties in this works. However, we restricted the application of the xLF/NSM to non-associating systems, because we used the Sanchez-Lacombe equation of state as a reference model. Research toward the application of the crossover equation of state to associating systems in progress using advanced lattice equation of state as a reference model, and future publications of our group will present the results.