R&D NOTE

Sufficiency Proof of $(V\text{-}V_c)^3 = 0$ at the Critical Point

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An explicit proof is presented showing that the method of equating coefficients between an equation of state (EOS), cubic in volume

$$V^3 + a_2(T,P)V^2 + a_1(T,P)V + a_0(T,P) = 0 \tag{1}$$

with those of

$$(V - V_c)^3 = 0 \tag{2}$$

is a corollary of the set of conditions

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0 \tag{3}$$

originally proposed by van der Waals, to analyze pure component behavior at the critical point (Van Ness and Abbott, 1982). This analysis is required to find an analytical form for the critical volume and two constants (appearing in the cubic EOS) in terms of T_c and P_c. The popularity of the method of equating coefficients results from the considerable algebraic manipulation that is required to solve Eq. 3 (in addition to EOS itself). Martin and Hou (1955) presented an implicit proof for the equivalence of the methods.

A more compact notation for Eq. 1

$$f(T,P,V) = 0 \tag{4}$$

is favored in this analysis, which starts by performing successive first- and second-order differentiation along an isotherm (with respect to volume)

$$\left(\frac{\partial f}{\partial P}\right)_{T,V}\left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial f}{\partial V}\right)_{T,P} = 0 \tag{5}$$

and

$$\left(\frac{\partial f}{\partial P}\right)_{T,V}\left(\frac{\partial^2 P}{\partial V^2}\right)_T + \left(\frac{\partial P}{\partial V}\right)_T\left[\left(\frac{\partial^2 f}{\partial P^2}\right)_{T,V}\left(\frac{\partial P}{\partial V}\right)_T + 2\frac{\partial^2 f}{\partial P \partial V}\right] + \left(\frac{\partial^2 f}{\partial V^2}\right)_{T,P} = 0 \tag{6}$$

At the critical point, these equations reduce to

$$\left(\frac{\partial f}{\partial V}\right)_{T=T_c, P+P_c} = \left(\frac{\partial^2 f}{\partial V^2}\right)_{T=T_c, P=P_c} = 0 \tag{7}$$

upon application of the constraints given by Eq. 3. The above analysis results in a set of constraints that are equivalent to and, more significantly, interchangeable with the set originally proposed by van der Waals. Application of Eq. 7 to Eq. 1 for the current example of a cubic EOS gives

$$\left(\frac{\partial f}{\partial V}\right)_{T=T_c, P=P_c} = 3V_c^2 + 2a_2V_c + a_1 = 0 \tag{8}$$

and

$$\left(\frac{\partial^2 f}{\partial V^2}\right)_{T=T_c, P=P_c} = 6V_c + 2a_2 = 0 \tag{9}$$

Solving Eqs. 9 and 8 sequentially yields

$$a_2 = -3V_c \tag{10}$$

and

$$a_1 = 3V_c^2 \tag{11}$$

Lastly, a_2 and a_1 are eliminated from Eq. 1 to find

$$a_0 = -V_c^3 \tag{12}$$

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Next, consider a term-by-term comparison with a cubic expansion of

$$(V - V_c)^3 = V^3 + (-3V_c)V^2 + (3V_c^2)V - V_c^3 = 0 \quad (13)$$

Because of the one to one correspondence between the coefficients in Eq. 13 with those given by Eqs. 10–12, this is an explicit proof of the equivalence of the methods, providing direct algebraic solutions for a_0, a_1, and a_2. Further, the analysis shows that a_2 is obtained from the second derivative, a_1 from the first derivative, and a_0 from the EOS itself.

For an EOS of higher degree, the corollary to solve these cases may be extended by equating the coefficients between the volume algebraic form of the EOS with those resulting from expanding

$$(V - V_c)^{n+1} = 0 \quad (14)$$

where $n+1$ must be an odd positive integer for physical reasons. The only requirement is that the original set of conditions proposed by van der Waals may be extended according to Martin and Hou (1955)

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = \cdots = \left(\frac{\partial^n P}{\partial V^n}\right)_{T=T_c} = 0 \quad (15)$$

to analyze the critical point.

In conclusion, an explicit proof has been presented confirming that the popular technique of equating coefficients between a cubic EOS with those of $(V - V_c)^3 = 0$ (at the critical point) is directly connected to the set of constraints proposed by van der Waals.

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Notation

P = abolute pressure
T = absolute temperature
V = molar volume

Subscript

c = critical point

Literature Cited

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