

# A Cubic Equation of State for High-Pressure Phase Equilibria of Mixtures Containing Polymers and Volatile Fluids

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## Synopsis

Generalized van der Waals theory is used to obtain a three-parameter cubic equation of state which is applicable to fluids containing small or large molecules, including polymers. The necessary parameters are obtained from a minimum of experimental information. Upon extension to mixtures, the equation of state is used to calculate high-pressure phase equilibria for the ethylene-polyethylene system. The relatively simple equation may be useful for engineering-design calculations for fluid mixtures containing polymers, especially when very few experimental data are available.

## INTRODUCTION

An equation of state (EOS) is a powerful tool for chemical process design. However, most existing EOS are applicable only to mixtures containing volatile fluids. While several authors have presented EOS that may also be used for fluids containing nonvolatile, large molecules such as polymers,<sup>1-3</sup> these equations are often complex and require molecular parameters that are not readily available. The purpose of this chapter is to present a simple, cubic EOS that is useful for both small and large molecules, and that requires a minimum of experimental information. We derive our EOS from the generalized van der Waals partition function coupled with Prigogine's and Beret's assumptions, and present a new method for calculating pure-component parameters in the EOS. We illustrate application with some calculations for high-pressure phase equilibria for the system ethylene-polyethylene.

## GENERALIZED VAN DER WAALS PARTITION FUNCTION

The generalized van der Waals partition function  $Q$  for a pure fluid is<sup>4</sup>

$$Q = \frac{1}{N!} \left[ \frac{V}{\Lambda^3} \right]^N \left[ \frac{V_f}{V} \right]^N \left[ \exp\left(\frac{-E_0}{2kT}\right) \right]^N [Q_{r,v}]^N \quad (1)$$

where  $N$  is the number of molecules in total volume  $V$  at temperature  $T$ ,  $\Lambda$  is the de Broglie wavelength depending only on temperature and molecular

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mass,  $V_f$  is the free volume,  $k$  is Boltzmann's constant, and  $E_0$  represents the potential field experienced by one molecule due to attractive forces from all others. The term  $(N!)^{-1}(V/\Lambda^3)^N$  gives the translational contribution of an ideal gas to the partition function. The second and third bracketed terms account for repulsive and attractive forces between molecules. The last term represents the contribution of rotational and vibrational degrees of freedom to the partition function.

To obtain a simple EOS, we assume that the free volume is represented by the approximation of van der Waals:

$$V_f = V - \frac{N}{N_A} b \quad (2)$$

where  $N_A$  is Avogadro's number and  $b$  is a parameter determined by molecular size. Although eq. (2) is theoretically valid only at low densities, it is commonly used because it yields a numerically convenient cubic equation of state. For the potential field, we use the Soave-Redlich-Kwong form<sup>5</sup> (see Appendix A):

$$E_0 = -\frac{2a}{N_A b} \ln\left(1 + \frac{N}{N_A} \frac{b}{V}\right) \quad (3)$$

where parameter  $a$  is dependent on temperature and parameter  $b$  is not. Following Prigogine,<sup>6</sup>  $Q_{r,\nu}$  is factored into an internal part and an external part:

$$Q_{r,\nu} = Q_{r,\nu(\text{int})} \cdot Q_{r,\nu(\text{ext})} \quad (4)$$

where  $Q_{r,\nu(\text{int})}$  depends only on temperature and  $Q_{r,\nu(\text{ext})}$  depends on density. Again following Prigogine, we assume further that the external rotational and vibrational degrees of freedom can be considered as equivalent translational degrees of freedom. Beret and Prausnitz<sup>1</sup> proposed a function for  $Q_{r,\nu(\text{ext})}$  which is consistent with Prigogine's assumption at liquid densities and with the ideal-gas law at low density:

$$Q_{r,\nu(\text{ext})} = \left(\frac{V_f}{V}\right)^{c-1} \quad (5)$$

where  $3c$  is the total number of external degrees of freedom per molecule.

The EOS is obtained from the partition function by

$$p = kT \cdot \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \quad (6)$$

Substitution of eqs. (1)–(5) into (6) gives a cubic EOS:

$$p = \frac{RT(\nu - b + bc)}{\nu(\nu - b)} - \frac{a}{\nu(\nu + b)} \quad (7)$$

where  $p$  is the pressure,  $\nu$  is the molar volume, and  $R$  is the gas constant.

When  $c = 1$ , eq. (7) reduces to the Soave-Redlich-Kwong EOS. The third parameter  $c$  extends the applicability of eq. (7) to systems containing large molecules.

If the potential field  $E_0$  is given by the expression of Peng and Robinson, an EOS similar to eq. (7) is obtained. However, in that event, the EOS is fourth order in volume, as discussed by Kubic.<sup>7</sup> For efficient computation, a cubic equation is often preferred since the roots of a cubic equation can be obtained analytically.

### EOS PARAMETERS FOR VOLATILE FLUIDS

For a volatile fluid, parameters  $a_{(T=T_c)}$  and  $b$  can be obtained upon using the conditions that, at the critical point,  $(\partial p/\partial V)_{T_c} = 0$  and  $(\partial^2 p/\partial V^2)_{T_c} = 0$ . We then obtain

$$a_{(T=T_c)} = a_c = \frac{(1 - 2D_0 + 2cD_0 + D_0^2 - cD_0^2)(1 + D_0)^2}{3(1 - D_0)^2(2 + D_0)} \cdot \frac{R^2 T_c^2}{p_c} \quad (8)$$

$$b = \frac{D_0}{3} \cdot \frac{RT_c}{p_c} \quad (9)$$

where  $D_0$  is a function of  $c$ :

$$D_0^3 + (6c - 3)D_0^2 + 3D_0 - 1 = 0 \quad (10)$$

Regardless of the value of  $c$ , eqs. (7)–(10) give a critical compressibility factor  $z_c = 1/3$ .

At temperatures other than  $T_c$ ,

$$a = a_c \alpha(T) \quad (11)$$

where  $\alpha(T)$  is a dimensionless function which becomes unity at  $T = T_c$ . Based on our study of the saturated and PVT properties of  $n$ -alkanes,<sup>8</sup> we propose

$$\alpha(T) = \frac{\alpha_0(1 - T_R^2) + 2T_R^2}{1 + T_R^2} \quad (12)$$

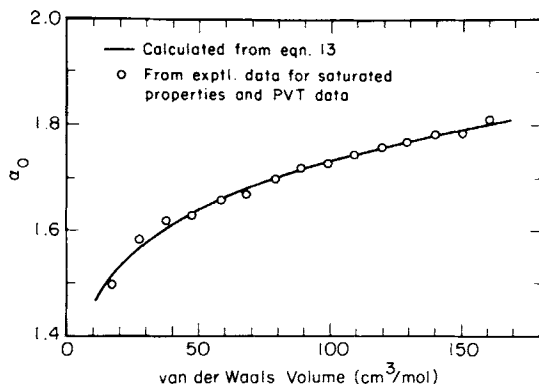
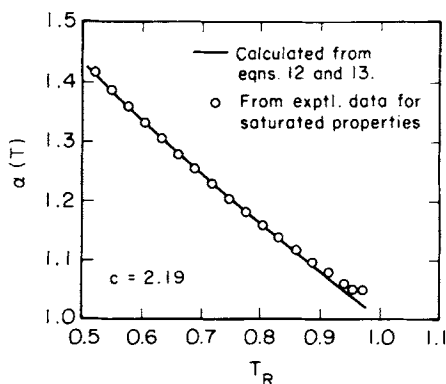
where the reduced temperature  $T_R$  is defined by  $T_R = T/T_c$  and  $\alpha_0$  is given by

$$\alpha_0 = 1.1920 + 0.11060 \cdot \ln(V_w) + 0.30734 \times 10^{-3} \cdot V_w \quad (13)$$

where van der Waals volume  $V_w$  (cm<sup>3</sup>/mol) is calculated by the group-contribution method of Bondi.<sup>9</sup>

The fugacity coefficient for a pure fluid is given by

$$\ln\left(\frac{f}{p}\right)_{\text{pure}} = -\ln\frac{p(v-b)}{RT} - \frac{a}{bRT} \ln\left(1 + \frac{b}{v}\right) + \left(\frac{pv}{RT} - 1\right) - \ln\left(\frac{v-b}{v}\right)^{c-1} \quad (14)$$

Fig. 1. Relation between  $\alpha_0$  and  $V_w$  for *n*-alkanes.Fig. 2. Plot of  $\alpha(T)$  vs.  $T_R$  for *n*-octane.TABLE I  
Calculated Saturated and PVT Properties for *n*-alkanes<sup>a</sup>

Fluid	Parameter <i>c</i>	Deviation from experiment (%)					
		New EOS			SRK EOS		
		$p^s$	$v_l^s$ or $v_l$	$v_g^s$	$p^s$	$v_l^s$ or $v_l$	$v_g^s$
CH <sub>4</sub>	1.00	2.16	5.22	2.77	1.68	5.52	1.80
C <sub>2</sub> H <sub>6</sub>	1.20	1.14	6.58	1.21	1.28	8.72	1.40
C <sub>3</sub> H <sub>8</sub>	1.34	1.22	6.97	1.83	0.73	10.51	1.37
C <sub>4</sub> H <sub>10</sub>	1.51	1.75	4.17	2.50	1.67	9.69	0.72
C <sub>5</sub> H <sub>12</sub>	1.68	1.82	5.98	1.98	1.48	12.76	1.25
C <sub>6</sub> H <sub>14</sub>	1.85	2.31	8.85	3.70	0.90	17.57	1.52
C <sub>7</sub> H <sub>16</sub>	2.02	2.23	7.50	2.80	2.00	16.89	2.64
C <sub>8</sub> H <sub>18</sub>	2.19	1.84	8.17	2.14	1.03	19.03	1.01
C <sub>9</sub> H <sub>20</sub>	2.36	0.40	1.00	0.40	0.71	15.79	0.66
C <sub>10</sub> H <sub>22</sub>	2.54	0.81	1.35	—	1.18	18.82	—
C <sub>11</sub> H <sub>24</sub>	2.71	1.08	1.55	—	1.39	19.57	—
C <sub>12</sub> H <sub>26</sub>	2.88	0.90	1.83	—	3.12	21.50	—
C <sub>13</sub> H <sub>28</sub>	3.05	2.40	1.73	—	1.69	21.25	—
C <sub>14</sub> H <sub>30</sub>	3.22	2.00	1.60	—	8.43	21.98	—
C <sub>15</sub> H <sub>32</sub>	3.39	3.02	1.98	—	1.88	23.63	—
Av. dev. (%)		1.67	4.30	2.15	1.94	16.22	1.37

<sup>a</sup> Calculations based on eqs. (8)–(14).

where the first three terms on the right-hand side are same as those of the Soave-Redlich-Kwong EOS and only the last term contains parameter  $c$ .

Figure 1 shows the relation between  $\alpha_0$  and  $V_w$  for  $n$ -alkanes from methane to pentadecane; the solid line gives results calculated by eq. (13), while the points show the best  $\alpha_0$  required to reproduce saturated and PVT properties. Figure 2 shows a plot of  $\alpha(T)$  vs.  $T_R$  for  $n$ -octane. The calculated line is obtained from eqs. (12) and (13), while the points were obtained from fitting saturated and PVT properties of  $n$ -octane. All of these calculations are based on values of  $c$  shown in Table I and Figure 3. This table also indicates that eqs. (7)–(13) are suitable for fitting the saturated and PVT properties of  $n$ -alkanes from methane to pentadecane.

### REFORMULATION OF EOS PARAMETERS FOR APPLICATION TO POLYMERS

Equations (8)–(13) are not useful for polymers because critical properties are not available. To apply eq. (7) to polymers as well as to volatile fluids, energy parameter  $a$  is determined from London's formula for dispersion forces<sup>10</sup> and volume parameter  $b$  is calculated using the van der Waals volume obtained from Bondi's method. Only parameter  $c$  is determined from density data.

To calculate parameter  $a$ , we assume that: (1) a polymer molecule can be divided into equal segments; (2) the potential energy between two adjacent, nonbonded segments is given by London's dispersion formula; and (3) the potential energy of the entire system is pairwise additive. When a polymer molecule consists of  $r$  segments, molar volume  $v$  and parameters  $a$ ,  $b$ ,  $c$  of the polymer are related to those of the segment by

$$\begin{aligned} a &= r^2 \cdot a' = r^2 [a'^* \cdot f'(\tilde{T})], & b &= r \cdot b' \\ c &= r \cdot c', & v &= r \cdot v' \end{aligned} \quad (15)$$

where ' represents segment basis and \* designates a close-packed system. The function  $f'(\tilde{T})$  depends on reduced temperature  $\tilde{T}$  which is the ratio of kinetic energy to potential energy per molecule:

$$\tilde{T} = ckT/\epsilon \quad (16)$$

where  $\epsilon$  is a potential-energy parameter per molecule. Parameter  $\epsilon$  (per molecule) is related to potential-energy parameter  $\epsilon'$  (per segment) by (Appendix B)

$$\epsilon = r \cdot \epsilon' = \left( \frac{9}{16\pi^2} \right) \frac{r}{N_A} \left( \frac{A'^2 \cdot I'}{V_w'^2} \right) \quad (17)$$

where  $A'$  is molar polarization of the segment ( $\text{cm}^3/\text{mol}$ ),  $I'$  is the first ionization potential of the segment ( $\text{cm}^3 \cdot \text{bar}/\text{mol}$ ), and  $V_w'$  is the van der Waals volume of the segment ( $\text{cm}^3/\text{mol}$ ).

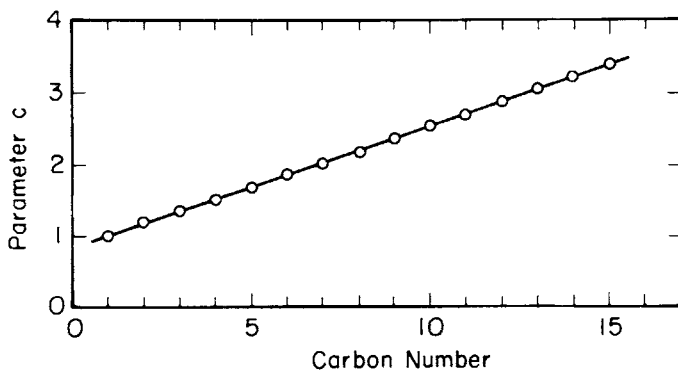


Fig. 3. Parameter  $c$  as a function of carbon number for  $n$ -alkanes.

As shown in Appendix B, parameter  $\alpha'^*$  in eq. (15) is written as

$$\alpha'^* = 0.1659 \cdot (A'^2 \cdot I'/V'_w) \quad (18)$$

Function  $f'(\tilde{T})$  is expected to have a universal form for  $n$ -alkanes and for linear chain polymers such as polyethylene. This function must meet two boundary conditions:  $f'(\tilde{T}) \rightarrow 1$  as  $\tilde{T} = 0$ , and  $f'(\tilde{T}) \rightarrow 0$  as  $\tilde{T} \rightarrow \infty$ . A simple function which satisfies these boundary conditions is

$$f'(\tilde{T}) = \exp(-a_0\tilde{T}) \quad (19)$$

where  $a_0$  is a constant determined by reduction of saturated-property and PVT data. Combining eqs. (15), (18), and (19) gives

$$a = 0.1659 \cdot \left( \frac{A'^2 \cdot I'}{V'_w} \right) \cdot r^2 \cdot \exp(-a_0\tilde{T}) \quad (20)$$

Volume parameter  $b$  is nearly proportional to the van der Waals volume. Figure 4 shows that, when  $b$  is determined from critical data using eq. (9), we

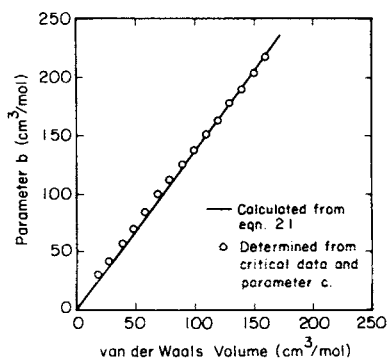


Fig. 4. Relation between parameter  $b$  and  $V_w$ .

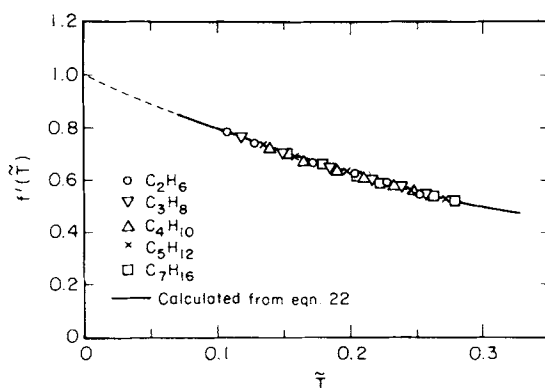


Fig. 5. Corresponding-states correlation for temperature-scaling function of parameter  $a'$ .

obtain

$$b = 1.3768V_w \quad (21)$$

Equation (21) is used to calculate  $b$  for polymers. As in eq. (13),  $V_w$  is obtained from Bondi's correlation.

Since parameter  $c$  is sensitive not only to molecular size but also to molecular structure, it is difficult to correlate this parameter with other properties. Therefore, for polymers, parameter  $c$  is determined from fitting density data over whatever range of temperature and pressure may be available.

#### Determination of $a_0$ in Eq. (20)

Parameters  $c$  and  $a_0$  and segment number  $r$  are determined from saturated and PVT properties for  $C_2$ ,  $n-C_3$ ,  $n-C_4$ ,  $n-C_5$ , and  $n-C_7$ . For a nonpolar compound, molar polarization  $A$  is equal to molar refraction. Molar refraction, in turn, can be calculated from group-contribution methods using atomic indices of refraction.<sup>11-14</sup> Van der Waals volume  $V_w$  is calculated using the group-contribution method of Bondi. First ionization potential  $I$  is obtained from Robinson.<sup>15</sup> Parameters  $c$ ,  $a_0$ , and  $r$  are fitted to the saturated volumetric data with the following conditions: (1)  $f'(\tilde{T})$  is the same for all compounds, and (2)  $(A'^2 \cdot I'/V_w')$  is equal to  $(1/r)(A^2 \cdot I/V_w)$  because  $A = r \cdot A'$ ,  $V_w = r \cdot V_w'$ , and  $I = I'$ , where  $A$ ,  $I$ , and  $V_w$  are the quantities on molecular basis.

Table II gives values of  $c$  and  $r$ , and identifies the physical properties required to calculate them. From a plot of  $f'(\tilde{T})$  vs.  $\tilde{T}$  shown in Figure 5, parameter  $a_0$  is determined:

$$f'(\tilde{T}) = \exp(-2.3731\tilde{T}) \quad (22)$$

#### Determination of Parameter $a$

For polymers, parameter  $a$  is determined by eq. (20). We obtain  $(A'^2I'/V_w')$  from data for the saturated monomer because the characteristic potential energy of the segment  $(A'^2I'/V_w'^2)$  is almost equal to  $(A^2I/V_w^2)$  of the

TABLE II  
Parameters in EOS and Physical Properties When Using Eqs. (15)–(21)<sup>a</sup>

	Parameters in EOS				Physical properties		
	$a'^* \times 10^{-6}$ (cm <sup>6</sup> bar/mol <sup>2</sup> )	$b$ (cm <sup>3</sup> /mol)	$c$	$r$	$A$ (cm <sup>3</sup> /mol)	$I \times 10^{-7}$ (cm <sup>3</sup> bar/mol)	$V_w$ (cm <sup>3</sup> /mol)
C <sub>2</sub> H <sub>6</sub>	7.777	37.64	1.18	1.10	11.28	1.109	27.34
C <sub>3</sub> H <sub>8</sub>	8.245	51.73	1.33	1.44	15.87	1.068	37.57
C <sub>4</sub> H <sub>10</sub>	8.593	65.81	1.52	1.78	20.86	1.013	47.80
C <sub>5</sub> H <sub>12</sub>	8.990	79.90	1.66	2.08	25.57	1.001	58.03
C <sub>7</sub> H <sub>16</sub>	9.795	108.1	1.86	2.60	34.99	0.9841	78.49

<sup>a</sup>Correlation for *n*-alkanes extends to the critical point for vapor pressure, liquid density, and vapor density (with relative weights 3:2:1) from methane to nonane, and for vapor pressure and liquid density at atmospheric pressure (with relative weights 3:2) from decane to pentadecane.

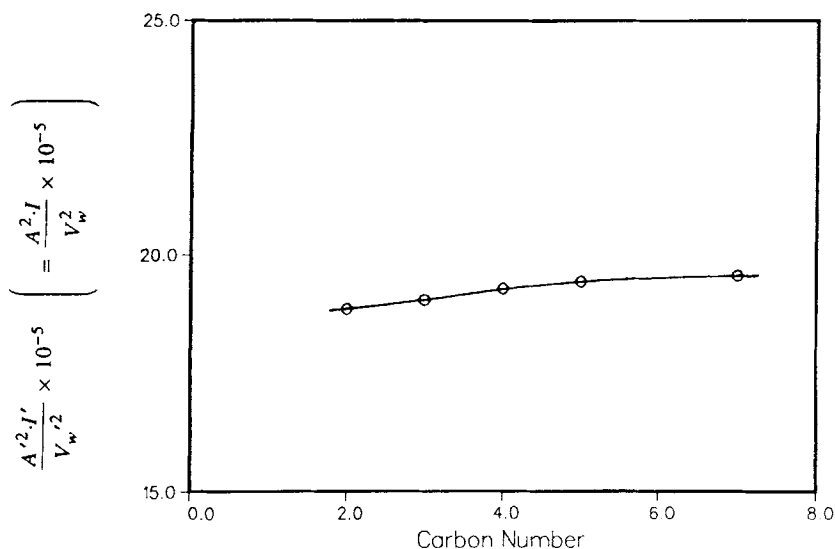


Fig. 6. Relation between characteristic potential energy per segment (cm<sup>3</sup> bar/mol) and chain length for *n*-alkanes.

saturated monomer. Figure 6 shows the relation between the characteristic energy of *n*-alkanes and the molecular chain length. Since this characteristic energy is almost constant, we assume that if molecules can be divided into equal segments, the characteristic energy per segment is also constant for a homologous series. This assumption is justified because  $A = r \cdot A'$ ,  $V_w = r \cdot V_w'$ , and  $I = I'$ . Similarly, we assume that the characteristic energy per segment of a polymer is equal to that of the saturated monomer. Thus, we have

$$\left( \frac{A'^2 I'}{V_w'^2} \right)_{\text{p.s.}} = \left( \frac{A'^2 I'}{V_w'^2} \right)_{\text{s.m.s.}} = \left( \frac{A^2 I}{V_w^2} \right)_{\text{sat.m.}} \quad (23)$$

where subscripts p.s., s.m.s., and sat.m. represent the segment of the polymer,



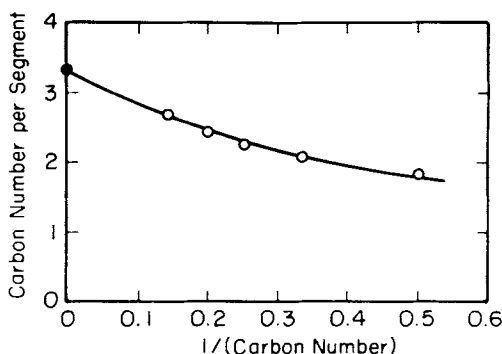


Fig. 7. Determination of carbon number per segment for polymers.

the segment of small molecules such as *n*-alkanes, and the saturated monomer, respectively. Therefore,

$$\left( \frac{A'^2 I'}{V_w'} \right) = \left( \frac{A^2 I}{V_w^2} \right)_{\text{sat.m.}} \cdot V_w' \quad (24)$$

Parameter  $\alpha_0$  in eq. (20) is assumed to be same as that for *n*-alkanes because the polymers treated in this work are chain molecules similar to *n*-alkanes. The final equation for parameter  $\alpha$  is

$$\alpha_{(\text{polymer})} = 0.1659 \cdot \left( \frac{A^2 I}{V_w^2} \right)_{\text{sat.m.}} \cdot V_{w(\text{polymer})} \cdot r \cdot \exp(-2.3731 \cdot \tilde{T}) \quad (25)$$

where  $V_{w(\text{polymer})}$  is calculated from molecular weight and from the structural formula of the repeating unit.

Segment number  $r$  is determined from the assumption that there are 3.33 carbon atoms per segment. This assumption is derived from fitting *n*-alkane data. Figure 7 shows a plot of carbon number per segment vs. inverse carbon number for *n*-C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, and C<sub>7</sub>. The extrapolation of the curve leads to the constant value 3.33 for very large molecules.

### Data Reduction for Polymers

We require the molecular weight to correlate PVT data for a polymer. However, a real polymer generally has a molecular-weight distribution and, therefore, three kinds of average molecular weight are in common use: number-average molecular weight, weight-average molecular weight, and viscosity-average molecular weight. As the number-average molecular weight is most closely related to thermodynamic properties,<sup>16</sup> we calculate the volumetric properties considering the polymer to be monodisperse with the number-average molecular weight.

Volumetric data are fitted for seven liquid polymers over a wide temperature and pressure range.<sup>17-20</sup> Calculated results are given in Table III; properties of the saturated monomers are presented in Table IV. The calcu-

TABLE III  
Calculated Results for Specific Volumes of Polymers

Polymer <sup>a</sup>	Range of PVT data		$\bar{M}_n$	Segment number	$(c/r)$	Deviation (%)
	$T$ (K)	$P$ (bar)				
PE	413-473	1-1000	25,000	535.3	0.57	1.42
PP	263-303	1-700	15,700	224.1	0.61	0.94
PIB	333-383	1-1000	36,000	385.4	0.41	0.61
PVC	355-370	1-1000	30,000	288.3	0.49	0.91
PVAC	333-393	1-1000	84,000	586.0	0.59	2.97
PS	413-469	1-800	90,700	523.0	0.57	3.45
POMS	432-471	1-800	90,700	460.9	0.49	3.56

<sup>a</sup>PE = polyethylene, PP = polypropylene, PIB = polyisobutylene, PVC = poly(vinyl chloride), PVAC = polyvinylacetate, PS = polystyrene, POMS = poly(*o*-methylstyrene).

TABLE IV  
Physical Properties of Saturated Monomers

Polymer	Saturated monomer	$A$ (cm <sup>3</sup> /mol)	$I \times 10^{-7}$ (cm <sup>3</sup> bar/mol)	$V_w$ (cm <sup>3</sup> /mol)
PE	Ethane	11.28	1.109	27.34
PP	Propane	15.87	1.068	37.57
PIB	Isobutane	20.67	1.040	47.79
PVC	Ethylchloride	16.30	1.062	36.14
PVAC	Ethylacetate	22.21	0.9880	52.77
PS	Ethylbenzene	35.54	0.8510	69.74
POMS	<i>o</i> -Methyl ethylbenzene	40.16	0.8153	80.89

lated volumes agree well with experiment for the first four polymers from the top of Table III. The other three polymers give a somewhat larger deviation, probably because the segments of these polymers deviate from spherical symmetry owing to the large phenyl or acetyl group. Figure 8 shows the relation between  $(c/r)$  and carbon number for *n*-alkanes and polyethylene. The value of  $(c/r)$  for polyethylene is on the extension of the line for *n*-alkanes, indicating that eq. (7) provides a reasonable model for polymeric fluids when the polymer is regarded as a homolog of the saturated monomer.

### Extension to Mixtures

When phase *L* is in equilibrium with phase *V* at the same temperature and pressure, the equilibrium condition is given by

$$x_i^L \cdot \phi_i^L \cdot p = y_i^V \cdot \phi_i^V \cdot p \quad (26)$$

where  $x$  and  $y$  are mole fractions in phases *L* and *V*, and  $\phi$  is the fugacity coefficient. To calculate fugacity coefficients from eq. (7), we require mixing rules for three parameters  $a$ ,  $b$ ,  $c$  and the segment number  $r$  in the EOS. We

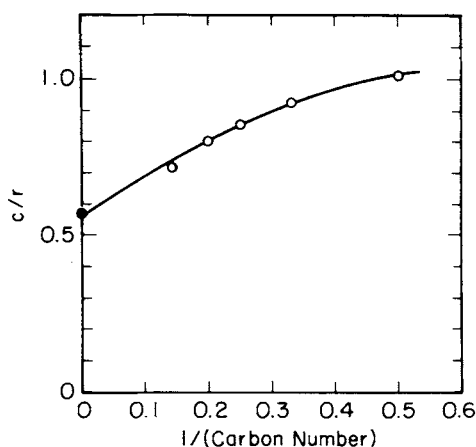


Fig. 8. Parameter  $c/r$  for  $n$ -alkanes and polyethylene.

assume one-fluid mixing rules:

$$\begin{aligned}
 a_m &= \sum_i \sum_j x_i x_j a_{ij} = \sum_i \sum_j x_i x_j r_i r_j a'_{ij} \\
 &= \sum_i \sum_j x_i x_j r_i r_j (1 - k'_{ij}) \sqrt{a'_{ii} a'_{jj}} \\
 b_m &= \sum_i x_i b_i = \sum_i x_i r_i b'_i \\
 c_m &= \sum_i x_i c_i = \sum_i x_i r_i c'_i \\
 r_m &= \sum_i x_i r_i
 \end{aligned} \tag{27}$$

where  $a_m$ ,  $b_m$ ,  $c_m$ , and  $r_m$  represent the mixture-parameters on a molecular basis;  $b_i$ ,  $c_i$ , and  $r_i$  are the pure-component parameters on a molecular basis;  $a'_{ii}$ ,  $b'_i$ , and  $c'_i$  are the pure-component parameters on a segment basis; and  $k'_{ij}$  is the binary interaction parameter between polymer segment  $i$  and solvent segment  $j$ .

From eqs. (7) and (27), the fugacity coefficient for component  $i$  in the mixture is given by

$$\begin{aligned}
 \ln \phi_i &= \frac{1}{RT} \int_v^\infty \left[ \left( \frac{\partial p}{\partial n_i} \right)_{T, v, n_j} - \frac{RT}{V} \right] dV - \ln z \\
 &= -\ln \frac{p(v - b_m)}{RT} - \frac{1}{RT} \left( \frac{2 \sum_j x_j a_{ij}}{b_m} - \frac{a_m b_i}{b_m^2} \right) \ln \left( 1 + \frac{b_m}{v} \right) \\
 &\quad - \frac{a_m b_i}{b_m RT (v + b_m)} + \frac{b_i c_m}{v - b_m} - \ln \left( \frac{v - b_m}{v} \right)^{c_i - 1}
 \end{aligned} \tag{28}$$

TABLE V  
Pure-Component Parameters on Segment Basis for Ethylene and Polyethylene

Component	$T$ (K)	Segment number	$a' \times 10^{-6}$ ( $\text{cm}^6 \text{ bar/mol}^2$ )	$b'$ ( $\text{cm}^3/\text{mol}$ )	$c'$
Ethylene	403.2	0.91	3.8737	36.13	1.23
Polyethylene	403.2	$\bar{M}_n \times 0.02141$	6.9917	46.90	0.57

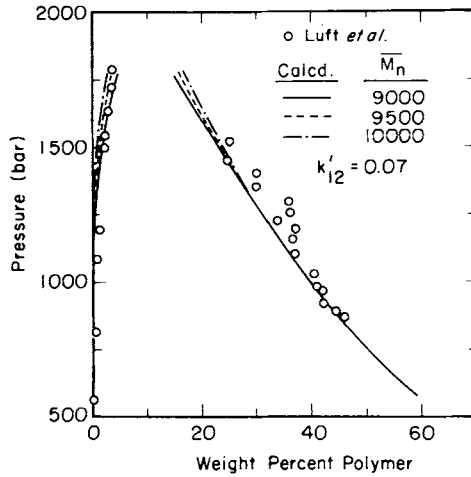


Fig. 9. Phase diagram for ethylene-monomer polyethylene system at 403.2 K.

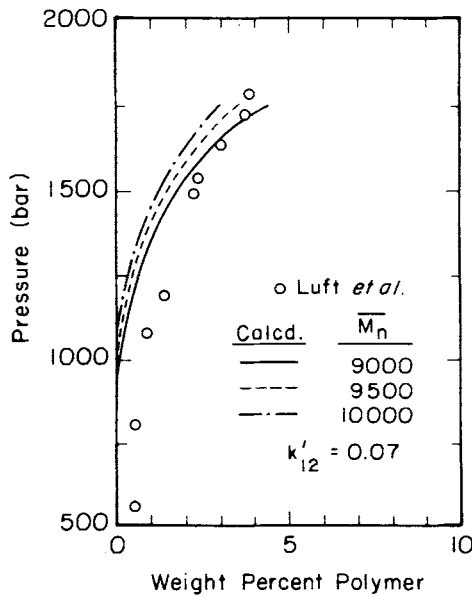


Fig. 10. Solubility of monodisperse polyethylene in ethylene at 403.2 K.

At a given temperature and pressure, equilibrium compositions in both phases can be calculated from eqs. (26)–(28) in addition to eq. (7).

### Phase Equilibria for Ethylene–Polyethylene

Phase equilibria are calculated for the system ethylene (1)–polyethylene (2) at 403.2 K using the numerical method presented by Bonner et al.<sup>21</sup> In this calculation, polyethylene is assumed to be monodisperse. Table V gives pure-component parameters on a segment basis for ethylene and polyethylene. Parameters for ethylene are obtained by fitting saturated properties and PVT properties to the EOS. Figures 9 and 10 show calculated results along with experimental data.<sup>22,23</sup> These figures also show the effect of the number-average molecular weight of polyethylene,  $\bar{M}_n$ , on the phase behavior.

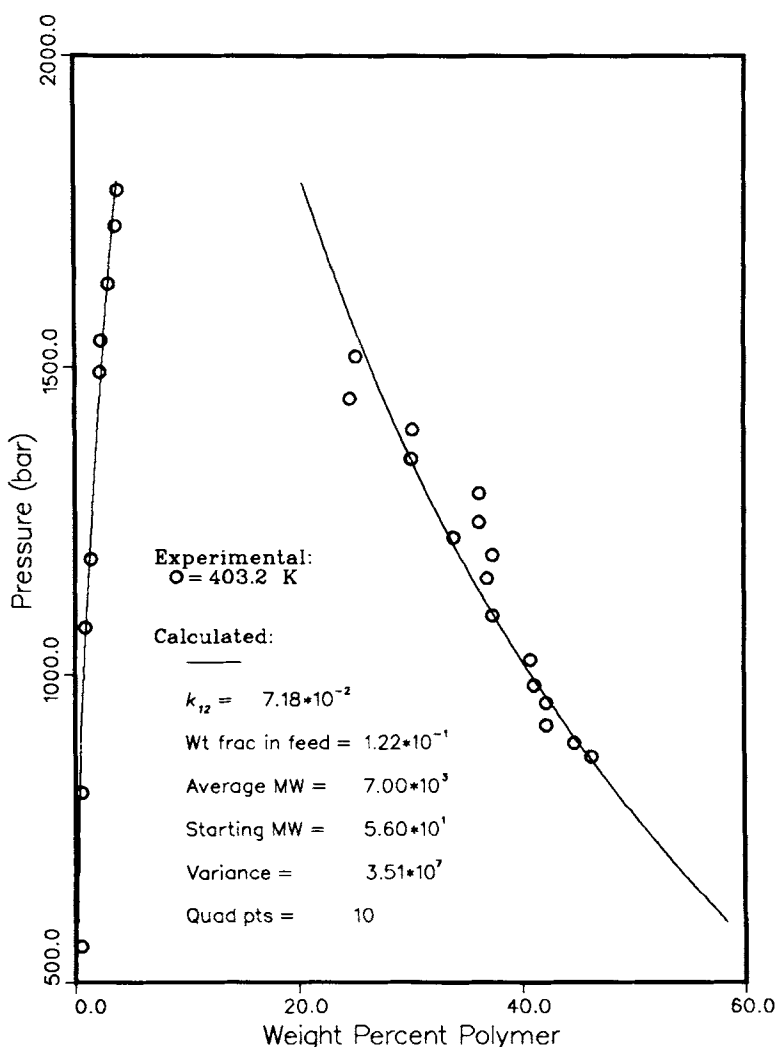


Fig. 11. Phase diagram for ethylene and polydisperse polyethylene at 403.2 K.

The best value of  $k_{12}$  is 0.07 for all calculations with different values of  $\bar{M}_n$ . The small positive value of  $k_{12}$  is reasonable because of the similarity in chemical nature and size between ethylene and a polymer segment. However, the value of  $k_{12}$  has a large effect on the phase diagram. When  $k_{12}$  is smaller than 0.06, the calculated critical pressure is below 1300 bar. On the other hand, a larger  $k_{12}$  causes a strong decrease in the concentration of polyethylene in the ethylene-rich phase.

The molecular weight of polyethylene also has an appreciable influence on the calculation. As the literature gives only the viscosity-average molecular weights (11,000 for the polyethylene-rich phase and 23,000 for the ethylene-rich phase), the calculation is made for three values of  $\bar{M}_n$ . The best calculated results are obtained when  $\bar{M}_n = 9000$ .

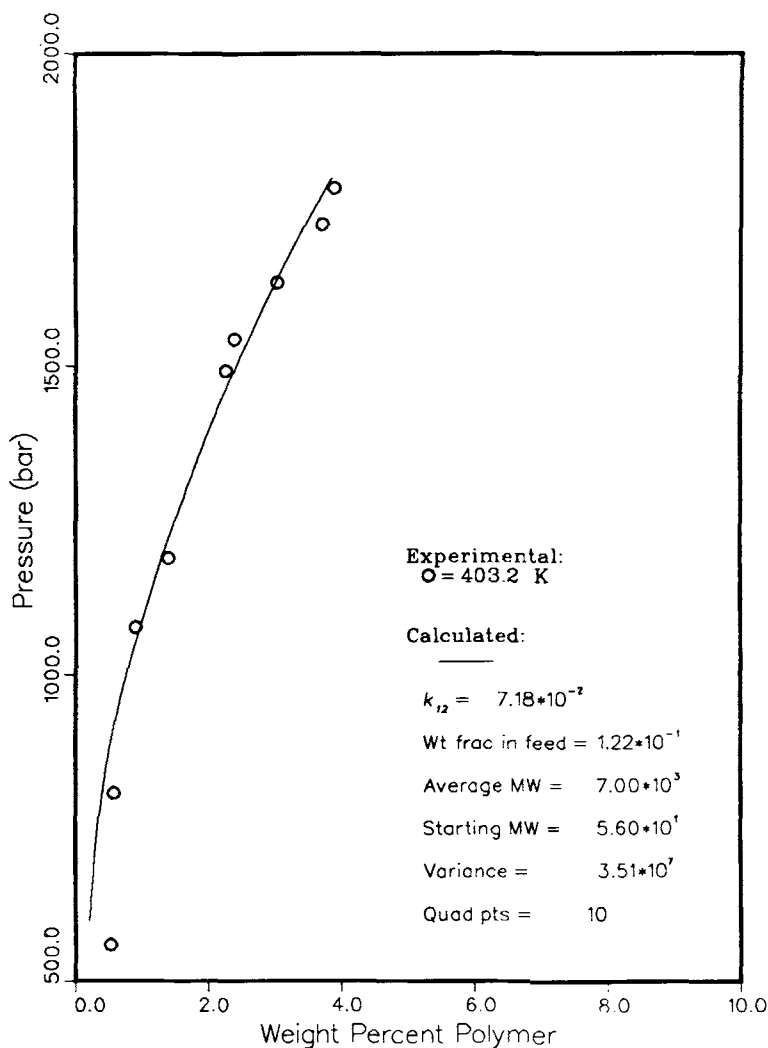


Fig. 12. Solubility of polydisperse polyethylene in ethylene at 403.2 K.

The calculated solubility of polyethylene in ethylene is very small at pressures below 1000 bar for all reasonable  $\bar{M}_n$ . As the system pressure approaches the critical pressure, the solubility increases steeply. The shape of the isothermal solubility curve for the ethylene-rich phase is highly sensitive to  $\bar{M}_n$  of polyethylene. On the other hand, the solubility curve for the polyethylene-rich phase is not sensitive to  $\bar{M}_n$ .

The calculated results indicate that if realistic calculations are to be made for both phases, it is necessary to take the molecular-weight distribution into consideration. In other words, it is not satisfactory to represent the heavy component (polyethylene) as a single component with some average molecular weight. Instead, it is necessary to represent the ethylene-polyethylene system as a multicomponent (not a binary) system.

Figures 11 and 12 show results for polydisperse polyethylene. The results are computed by using the Laguerre-Gaussian quadrature method with 10 quadrature points.<sup>24,25</sup> Continuous thermodynamics has also been applied to calculate phase behavior in the high-pressure ethylene-polyethylene system by Rätzsch and Kehlen.<sup>26,27</sup> As shown in Figures 11 and 12, calculated results agree much better with experiment in both vapor and liquid phases than results from the assumption of monodispersity. Figure 13 shows the hypothetical polymer distribution in the feed. The molecular-weight distribution is assumed to be a gamma distribution, with a number-average molecular weight of 7000 and a weight-average molecular weight of 12,000. This semiinfinite molecular-weight distribution is assumed to start at a molecular weight of 56 (molecular weight of dimers). The results of flash calculation are not very sensitive to the exact starting point of the molecular-weight distribution. For

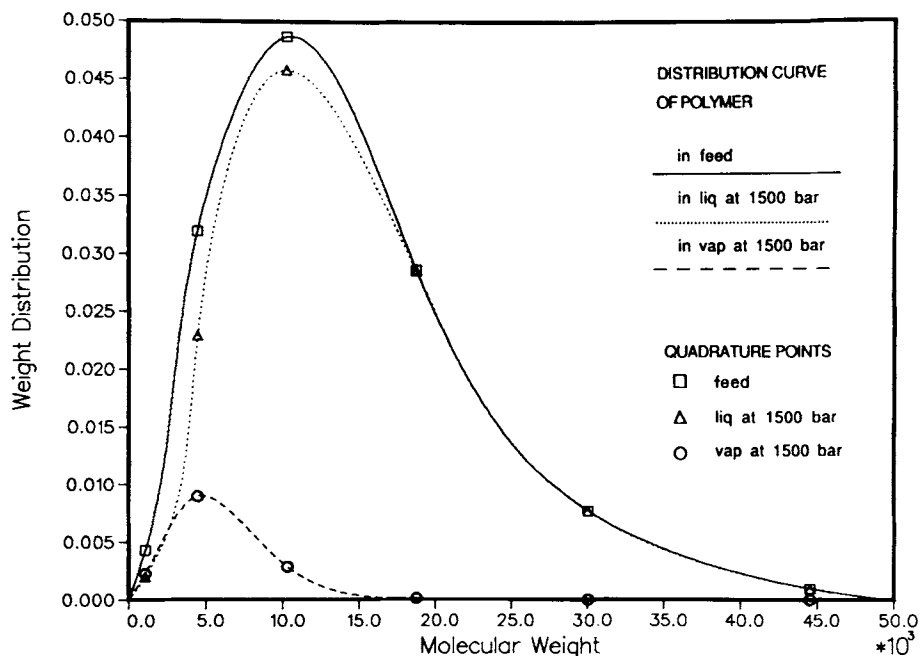


Fig. 13. Weight distributions of polydisperse polyethylene.

example, similar results are obtained if the starting point is 560 instead of 56. The resulting polymer distributions in the vapor phase and in the liquid phase at 1500 bar are also shown in Figure 13. The feed is assumed to contain 12.2 wt % of polymer. The binary interaction parameter between ethylene and polymer,  $k_{ij}$ , is assumed to be independent of molecular weight.

### CONCLUSION

A new cubic EOS has been derived from the generalized van der Waals partition function. The resulting three-parameter EOS is applicable to fluids containing small and large molecules.

The EOS was used to correlate volumetric data of *n*-alkanes. The results demonstrated the new EOS to be as good or better than the Soave-Redlich-Kwong EOS. To extend the proposed EOS to fluids containing very large molecules (polymers), a new method was developed for determining pure-component parameters. This method uses two adjustable parameters,  $r$  and  $c'$ , for volatile fluids, and only one adjustable parameter  $c'$  for polymers. The EOS gave a good correlation of volumetric data for seven polymers.

Phase-equilibrium calculations were made for the system ethylene-polyethylene at 403.2 K, using the proposed EOS and one-fluid mixing rules with one adjustable binary parameter  $k_{ij}$ . When the system is considered to be a pseudo-binary, calculated results for the polymer-rich phase are in good agreement with experiment but those for the ethylene-rich phase are only semiquantitative. However, calculations are in good agreement with experimental data for both the polymer-rich phase and the ethylene-rich phase when the polymer is considered as polydisperse.

The main advantage of this new EOS follows from its applicability to high-pressure polymer-solvent systems with a minimum of experimental information. Accuracy is probably not as high as that obtained with "better" equations of state which often require extensive experimental measurements. Thanks to the generalization of some of the equation's parameters, this new EOS can be used to estimate phase equilibria for those cases where experimental data are sparse.

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### APPENDIX A: POTENTIAL FIELD $E_0$ PROPOSED BY SOAVE

From statistical thermodynamics, the partition function for attractive contribution  $Q_a$  is directly related to the attractive term of an equation of state  $p_a$ :

$$\ln Q_a = -NE_0/2kT = \int \frac{P_a}{kT} dV \quad (29)$$

When the attractive term proposed by Soave is used,<sup>5</sup> we obtain

$$p_a = -\frac{a \cdot N^2}{N_A^2 V^2 + bN_A NV} \quad (30)$$



Substitution of eq. (30) into eq. (29) with the boundary condition  $\ln Q_a \rightarrow 0$  as  $V \rightarrow \infty$  gives

$$\ln Q_a = \frac{aN}{kTbN_A} \ln \left( 1 + \frac{N}{N_A} \frac{b}{V} \right) \quad (31)$$

or

$$E_0 = - \frac{2a}{N_A b} \ln \left( 1 + \frac{N}{N_A} \frac{b}{V} \right) \quad (32)$$

## APPENDIX B: DERIVATION OF EQS. (17) AND (18)

If eq. (3) is applied to a close-packed system, we obtain

$$\begin{aligned} a'^* &= - \frac{N_A b'}{2} \cdot \frac{1}{\ln(1 + Nb'/N_A V'^*)} \cdot E_0'^* \\ &= - \frac{N_A b'}{2} \cdot \frac{1}{\ln(1 + b'/v'^*)} \cdot E_0'^* \end{aligned} \quad (33)$$

where  $E_0'^*$  is the potential field experienced by one segment in a close-packed system at volume per segment  $V'^*$ .

From London's dispersion model for nonpolar molecules, the attractive potential energy between two simple, spherically symmetric molecules  $k$  and  $l$  is<sup>4</sup>

$$E_{kl}^* = - \frac{3}{2} \frac{\alpha_k \alpha_l}{r^6} \left( \frac{i_k i_l}{i_k + i_l} \right) \approx - \frac{3}{4} \frac{\alpha^2 i}{r^6} \quad (34)$$

where  $r$  is the distance between the two molecules. The molecular polarizability  $\alpha$  and molecular ionization potential  $i$  of molecule  $k$  are equal to those of molecule  $l$  if the two molecules are similar.

In a close-packed system, the distance  $r$  between two neighboring molecules is equal to molecular diameter  $d$ . The attractive potential energy of a molecule with respect to all of the others is given by<sup>4</sup>

$$E_0^* = \frac{zs_m}{d^6} \left( - \frac{3}{4} \alpha^2 i \right) = - \frac{3}{4} \alpha^2 i z s_m \frac{1}{d^6} \quad (35)$$

where  $z$  is the coordination number of the molecule,  $s_m$  is the packing constant, and \* denotes a close-packed system. Ionization potential (per molecule)  $i$  can be related to ionization potential (per mole)  $I$  by

$$I = N_A i \quad (36)$$

Molecular polarizability  $\alpha$  can be related to molar polarization  $A$  by<sup>12</sup>

$$A = (4\pi/3) N_A \alpha \quad (37)$$

By combining eqs. (35)–(37), we obtain

$$E_0^* = - \frac{27}{64\pi^2} \frac{A^2 I}{N_A^3} \frac{z s_m}{d^6} \quad (38)$$

If we apply Equation (38) to a system based on segments instead of molecules, we obtain

$$E_0'^* = - \frac{27}{64\pi^2} \frac{A'^2 I'}{N_A^3} z' s_m' \frac{1}{d'^6} \quad (39)$$

where ' denotes segment basis. For a face-centered-cubic lattice,  $z' = 12$ , and  $s_m' = 1.2045$ . For a close-packed system, the fraction of space occupied by molecules of diameter  $d'$  is<sup>28</sup>

$$\frac{V_w'}{v'^*} = \left( \frac{\pi d'^3}{6} \right) \cdot \left( \frac{\sqrt{2}}{d'^3} \right) = 0.7405 \quad (40)$$

Van der Waals volume is related to the volume of a spherical segment by

$$\frac{V_w'}{N_A} = \frac{\pi d'^3}{6} \quad (41)$$

If eq. (21) is applied to a close-packed system, we obtain

$$b' = 1.3768V_w' \quad (42)$$

Combining eqs. (33), (39)–(42) with the values for  $z'$  and  $s_m'$ , we obtain

$$\alpha'^* = 0.1659 \cdot \frac{A'^2 \cdot I'}{V_w'} \quad (43)$$

From Lennard–Jones potential and London's dispersion model for nonpolar molecules, the potential-energy parameter  $\epsilon'$  (per segment) can be expressed as

$$\epsilon' \approx \frac{\alpha'^2 \cdot i'}{(V_w'/N_A)^2} \quad (44)$$

By combining eqs. (36), (37), and (44), we obtain

$$\epsilon' = \left( \frac{9}{16\pi^2} \right) \frac{1}{N_A} \left( \frac{A'^2 \cdot I'}{V_w'^2} \right) \quad (45)$$

### APPENDIX C: NOMENCLATURE

$A$	molar polarization (cm <sup>3</sup> /mol)
$a$	energy parameter in EOS (cm <sup>6</sup> bar/mol <sup>2</sup> )
$a_0$	constant in eq. (19)
$b$	volume parameter in EOS (cm <sup>3</sup> /mol)
$3c$	total number of external degrees of freedom per molecule
$D_0$	constant determined from parameter $c$ using eq. (10)
$d'$	diameter of segment (cm)
$E_0$	potential field (cm <sup>3</sup> bar/molecule)
$f'(\bar{T})$	dimensionless temperature scaling function of $a'$ in eqs. (15) and (19)
$I$	first ionization potential per mole (cm <sup>3</sup> bar/mol)
$i$	first ionization potential per molecule (cm <sup>3</sup> bar/molecule) (Appendix B only)
$k$	Boltzmann's constant (cm <sup>3</sup> bar/molecule K)
$k_{i,j}$	binary interaction parameter
$\bar{M}_n$	number-average molecular weight of polymer
$N$	number of molecules
$N_A$	Avogadro's number

$n$	number of moles
$p$	pressure (bar)
$Q$	canonical partition function
$Q_a$	partition function for attractive term
$Q_{r,v}$	partition function for rotational and vibrational degrees of freedom
$R$	gas constant ( $\text{cm}^3 \text{ bar/mol K}$ )
$r$	segment number per molecule
$s'_m$	constant determined from crystal structure
$T$	temperature (K)
$T_R$	reduced temperature defined by $T_R = T/T_c$
$\bar{T}$	reduced temperature defined by eq. (16)
$V$	volume ( $\text{cm}^3$ )
$V_f$	free volume ( $\text{cm}^3$ )
$V_w$	van der Waals volume ( $\text{cm}^3/\text{mol}$ )
$v$	molar volume ( $\text{cm}^3/\text{mol}$ )
$x, y$	mole fractions
$z$	compressibility factor
$z'$	coordination number of segment
$\alpha$	molecular polarizability ( $\text{cm}^3/\text{molecule}$ ) (Appendix B only)
$\alpha$	dimensionless temperature-dependent function for parameter $a$ , defined in eqs. (11) and (12)
$\alpha_0$	parameter defined in eqs. (12) and (13)
$\epsilon$	characteristic energy ( $\text{cm}^3 \text{ bar/molecule}$ )
$\Lambda$	de Broglie wavelength (cm)
$\phi$	fugacity coefficient

### Subscripts

$a$	attractive term of EOS
$c$	critical property
ext	external
int	internal
$i, j$	index of components
$m$	mixture
p.s.	segment of polymer
s.m.s.	segment of small molecules such as $n$ -alkanes
sat.m.	saturated monomer

### Superscripts

$L, V$	index of phases
'	segment basis
*	close-packed system

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