Semiempirical equation of state for polymers and simple liquids: 2. Temperature and volume dependence of thermal pressure coefficient

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The temperature and volume dependence of the thermal pressure coefficient γ_v have been examined using experimental data on γ_v for simple liquids argon and water based on the equation of state derived in a previous work. The expression for $\tilde{\gamma}_v$ is given by $\tilde{\gamma}_v V \sim [\{(T_c - T)/T\}^{\delta_0} + C_0]X^{\beta_0} \exp(\alpha_0^{-1} I_0)$ where $\tilde{\gamma}_v = \gamma_v - \gamma_{v,c}$, T_c is the critical temperature and I_0 is defined by $I_0 = \int_{V_c}^{V} X^{\beta_0}/V \, dV$ where $X = (V_c - V)/V$ and V_c is the critical volume. The heat capacity at constant volume C_v is given by $C_v \sim C_v(T) - [\{(T_c - T)/T\}^{\delta_0 - 1}/T] \times \alpha_0 \exp(\alpha_0^{-1} I_0)$ where $C_v(T)$ is a function of temperature. Values of $\alpha_0, \beta_0, \delta_0$ and C_0 are constants. The equation of state for simple liquids is expressed using $Y = (T_c - T)/T$ by

$$\tilde{P} = (X^{\beta_0}/V)\left[\left\{T(Y^{\delta_0} + C_0) - \int_0^Y Y^{\delta_0 - 1}/(1 + Y)\,dY\right\}\exp(\alpha_0^{-1} I_0) - D_0 \exp(a_0^{-1} I_0)\right]$$

where D_0 is a constant. The temperature dependence of γ_v at constant volume for polymers is examined based on the experimental data by Simha and is given by $\gamma_v \sim T^{k_0 - 1}$ and $\bar{k}_0$ is -0.24 for polystyrene and poly(n-butyl methacrylate) and 2.8 for polymethyl methacrylate. The equation of state for a polymer is derived by the same procedure as for a simple liquid and is given by

$$P = C_2'(T)(Z^{\tau_0}/V)T \exp(\alpha_0'^{-1} I_{z,\tau_0}) - C_1'(T)(Z^{\lambda_0}/V)\exp(a_0'^{-1} I_{z,\lambda_0})$$

where $Z = (V - V_0)/V$, $I_{z,x_0} = \int_0^V Z^{x_0}/V \, dV$, $C_i'(T)$ is a function of temperature, τ_0, λ_0, a_0' and α_0' are constants and V_0 is a constant volume at 0 K. The expression for γ_v is given by $\tilde{\gamma}_v' V \sim Z^{\tau_1}$ where τ_1 is a constant. The values of τ_1 determined by the experimental data are -1.89 for polystyrene, -1.64 for polyisobutylene and -2.67 for polydimethyl siloxane. An essential difference between polymers and simple liquids is discussed in terms of the functional form of the equation of state. A characteristic feature of the volume dependence of entropy and internal energy is discussed through the experimental data on γ_v over a wide range of temperature and pressure.

(Keywords: equation of state; polymer; simple liquids, thermal pressure coefficient; heat capacity at constant volume)

INTRODUCTION

The equation of state for polymers and simple liquids is the most fundamental tool used in characterizing and predicting the thermomechanical and thermodynamical properties of pure liquids and liquid–liquid mixtures over a wide range of pressure and temperature. The most famous equation of state for liquids was derived by van der Waals[1]:

$$PV/T = VR/(V - b) - a/VT \tag{1}$$

where a and b are constant and R is the gas constant. Equation (1) is expressed in a more general form by

$$P/T = f(V) - g(V)/T \tag{2}$$

Most equations of state derived by other authors[2–8] have a functional form similar to equation (2) although $f(V)$ and $g(V)$ depend on the model used for the entropy and intermolecular energy of the liquid. In the Flory theory[2] of corresponding states the Tonks model for the entropy and the van der Waals model for intermolecular energy are used, while in the Simha–Somcynsky theory the hole model and the square-well approximation to the cell potential are used[4]. In a previous work we examined the Flory equation of state and found that the van der Waals model and Tonks model are useful only over a limited temperature range below the boiling point of the liquid[9] and proposed a semi-empirical equation of state for polymers and simple liquids in non-critical and critical regions from the standpoint of the homogeneous function approach[10]. Many authors, such as Bridgman[11], Gibson[12–14], Scott[15] and Foulkes[16], have examined the van der Waals equation of state experimentally and theoretically and found that the thermal pressure coefficient γ_v depends on temperature at constant volume, which does not agree with the prediction of van der Waals' equation that γ_v depends on volume only. Experimental results on γ_v suggest the following equation:

$$P/T = h(V, T) - m(V, T)/T \tag{3}$$

where both $h(V, T)$ and $m(V, T)$ are functions of volume and temperature.

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The main purpose of this work is to determine the functions $h(V, T)$ and $m(V, T)$ by using the experimental data and an equation of state derived by the homogeneous function method. An essential difference between polymers and simple liquids is discussed in terms of the equation of state.

DERIVATION OF EQUATION OF STATE BASED ON THE HOMOGENEOUS FUNCTION METHOD

In previous work[10,17,18] we derived an equation of state based on the following assumptions for internal energy E and entropy S: $E = E(V) + E(T)$, $S = S(V) + S(T)$. We determined that the thermal pressure coefficient γ_v is a function of volume[10] and the heat capacity at constant volume C_v is a function of temperature only[18] and, therefore, $(\partial\gamma_v/\partial T)_v = 0$ and $(\partial C_v/\partial V)_T = 0$.

In this work we assumed the following equations for $\tilde{E}$ and $\tilde{S}$ to explain the negative $(\partial\gamma_v/\partial T)_v$ and negative $(\partial C_v/\partial V)_T$ observed:

$$\tilde{E} = E - (\gamma_{v,c}T - P_c)V \tag{4}$$

$$= \tilde{E}_I(V, T) + \tilde{E}_{II}(T) \tag{5}$$

$$\tilde{S} = S - \gamma_{v,c}V \tag{6}$$

$$= \tilde{S}_I(V, T) + \tilde{S}_{II}(T) \tag{7}$$

where a subscript c refers to a value at the critical point. $\tilde{E}$ and $\tilde{S}$ represent the internal energy and entropy determined by taking the critical point as a reference state and are expressed as the sum of two terms, one a function of volume and temperature and the other a function of temperature only. Then we assumed that $\tilde{E}_I(V, T)$ and $\tilde{S}_I(V, T)$ are expressed by a homogeneous function of $V/(V_c - V)$ as

$$\tilde{E}_I(V, T) = a_0(\tilde{\gamma}_v T - \tilde{P})V\{V/(V_c - V)\}^{b_0} \tag{8}$$

$$\tilde{S}_I(V, T) = \alpha_0\tilde{\gamma}_v V\{V/(V_c - V)\}^{\beta_0} \tag{9}$$

where a_0, b_0, α_0 and β_0 are constants.

The following equations are also obtained from equations (4) and (5):

$$(\partial\tilde{E}/\partial V)_T = \gamma_v T - P - (\gamma_{v,c}T - P_c) = \tilde{\gamma}_v T - \tilde{P} \tag{10}$$

where $\tilde{P} = P - P_c$ and $\tilde{\gamma}_v = \gamma_v - \gamma_{v,c}$. From equation (6)

$$(\partial\tilde{S}/\partial V)_T = \gamma_v - \gamma_{v,c} = \tilde{\gamma}_v \tag{11}$$

The equation of state is given from equations (10) and (11) by

$$\tilde{P} = (\partial\tilde{S}/\partial V)_T T - (\partial\tilde{E}/\partial V)_T \tag{12}$$

The following equations are derived through the same procedure as in Reference 10:

$$\tilde{\gamma}_v T - \tilde{P} = C_1(T)(X^{b_0}/V)\exp\left\{a_0^{-1}\int_{V_c}^{V} X^{b_0}/V\,\mathrm{d}V\right\} \tag{13}$$

where $C_1(T)$ is a function of temperature, $X = (V_c - V)/V$ and

$$\tilde{\gamma}_v = C_2(T)(X^{\beta_0}/V)\exp\left\{\alpha_0^{-1}\int_{V_c}^{V} X^{\beta_0}/V\,\mathrm{d}V\right\} \tag{14}$$

where $C_2(T)$ is a function of temperature. The equation of state is derived as

$$\tilde{P} = C_2(T)T(X^{\beta_0}/V)\exp\left\{\alpha_0^{-1}\int_{V_c}^{V} X^{\beta_0}/V\,\mathrm{d}V\right\} - C_1(T)(X^{b_0}/V)\exp\left\{a_0^{-1}\int_{V_c}^{V} X^{b_0}/V\,\mathrm{d}V\right\} \tag{15}$$

The main difference between this and previous work is in the use of $C_1(T)$ and $C_2(T)$ instead of constants C_0 and C_1 (Reference 10). By taking a derivative of equation (15) with respect to temperature at constant P, it is derived that

$$\tilde{\gamma}_v T\left[T^{-1} + \frac{d\ln\{C_2(T)/C_1(T)\}}{\mathrm{d}T} + (b_0 - \beta_0)V_c\alpha_p/VX + \frac{\mathrm{d}\ln(I_{\beta_0}/I_{b_0})}{\mathrm{d}V}V\alpha_p\right] + \tilde{P}\left\{\frac{\mathrm{d}\ln C_1(T)}{\mathrm{d}T} - (b_0V_c/VX + 1)\alpha_p + \frac{\mathrm{d}\ln I_{b_0}}{\mathrm{d}V}V\alpha_p\right\} = 0 \tag{16}$$

where $I_{b_0} = \exp(a_0^{-1}\int_{V_c}^{V} X^{\beta_0}/V\,\mathrm{d}V)$, $I_{\beta_0} = \exp(\alpha_0{}^{-1}\int_{V_c}^{V} X^{\beta_0}/V\mathrm{d}V)$ and $\alpha_p = (\partial\ln V/\partial T)_p$. By using an approximation that $\tilde{\gamma}_v T \gg \tilde{P}$, equation (16) reduces to

$$(\alpha_p T)^{-1} + \frac{\mathrm{d}\ln\{C_2(T)/C_1(T)\}}{\mathrm{d}T}\alpha_p^{-1} + V_c(b_0 - \beta_0)/VX + V\left\{\frac{\mathrm{d}\ln(I_{\beta_0}/I_{b_0})}{\mathrm{d}V}\right\} = 0 \tag{17}$$

By considering the limiting case $\lim_{T\to T_c}\alpha_p \to \infty$, equation (17) is expressed by

$$(\alpha_p T)^{-1} = (a_0^{-1} - \alpha_0^{-1})X^{\beta_0} - \alpha_p^{-1}\frac{\mathrm{d}\ln\{C_2(T)/C_1(T)\}}{\mathrm{d}T} \tag{18}$$

where the equation $\beta_0 = b_0$ is used, which is obtained from $(\alpha_p T)^{-1} \to 0$ in the limit $T \to T_c$. It is also obtained from equations (14) and (15) and $(\partial\tilde{P}/\partial T)_V = (\partial P/\partial T)_V - \lim_{T\to T_c}(\partial P/\partial T)_V = \gamma_v - \gamma_{v,c} = \tilde{\gamma}_v$ that

$$T\exp(\alpha_0^{-1}I_0)\left(\frac{\mathrm{d}C_2(T)}{\mathrm{d}T}\right) = \exp(a_0^{-1}I_0)\left(\frac{\mathrm{d}C_1(T)}{\mathrm{d}T}\right) \tag{19}$$

where I_0 is defined by $I_0 = \int_{V_c}^{V} X^{\beta_0}/V\,\mathrm{d}V$ and V_c in the integration range means $\lim_{T\to T_c} V$.

Expressions for $\tilde{E}$ and $\tilde{S}$ are obtained from equations (5), (7), (8), (9), (13) and (14) as follows:

$$\tilde{E} = a_0C_1(T)\exp(a_0^{-1}I_0) + \tilde{E}_{II}(T) \tag{20}$$

and

$$\tilde{S} = \alpha_0C_2(T)\exp(\alpha_0^{-1}I_0) + \tilde{S}_{II}(T) \tag{21}$$

From $(\partial\tilde{E}/\partial T)_v = T(\partial\tilde{S}/\partial T)_v - \gamma_{v,c}V$, obtained from equations (4) and (6), and the thermodynamic relation $(\partial E/\partial T)_v = T(\partial S/\partial T)_v$, a relation at $V = \text{const.}$ is obtained as

$$a_0\frac{\mathrm{d}C_1(T)}{\mathrm{d}T}\exp(a_0^{-1}I_0) + \frac{\mathrm{d}\tilde{E}_{II}(T)}{\mathrm{d}T} + \gamma_{v,c}V = T\left\{\alpha_0\frac{\mathrm{d}C_2(T)}{\mathrm{d}T}\exp(\alpha_0^{-1}I_0) + \frac{\mathrm{d}\tilde{S}_{II}(T)}{\mathrm{d}T}\right\} \tag{22}$$

It is very interesting to derive C_v from γ_v using the thermodynamic equation

$$(\partial C_v/\partial V)_T = T(\partial\gamma_v/\partial T)_V \tag{23}$$

and, therefore,

$$C_v = \int T(\partial \gamma_v/\partial T)_v \, dV + C_v(T) \qquad (24)$$

where $C_v(T)$ is an integration constant and a function of temperature. Using the relation $(\partial \gamma_v/\partial T)_v = (\partial \tilde{\gamma}_v/\partial T)_v$ and equation (14), C_v is given by

$$C_v = T\{dC_2(T)/dT\}\alpha_0 \exp(\alpha_0^{-1} I_0) + C_v(T) \qquad (25)$$

EXPERIMENTAL DATA ON TEMPERATURE DEPENDENCE OF γ_v AT CONSTANT VOLUME AND VOLUME DEPENDENCE OF C_v AT CONSTANT TEMPERATURE

Typical data for the pressure–temperature curve at constant volume for polymers[19,20] poly(n-butyl methacrylate) (PNBMA) and poly(methyl methacrylate) (PMMA) are shown in *Figure 1*, where values of $(\partial P/\partial T)_v$ for PNMBA decrease and those for PMMA increase slightly with increasing temperature at constant volume. The P–T line at constant volume is expressed by

$$P = A_0 T^{k_0} + B_0 \qquad V = \text{const.} \qquad (26)$$

Values of A_0, k_0 and B_0 obtained by the best fitting to the data are listed in *Table 1*. In *Figure 2* experimental data on γ_v for argon[21] are plotted against temperature at constant volume. γ_v decreases with increasing temperature.

The volume dependence of C_v at constant temperature for argon[21] is shown in *Figure 3*. C_v decreases with increasing volume or increases with increasing $X = (V_c - V)/V$.

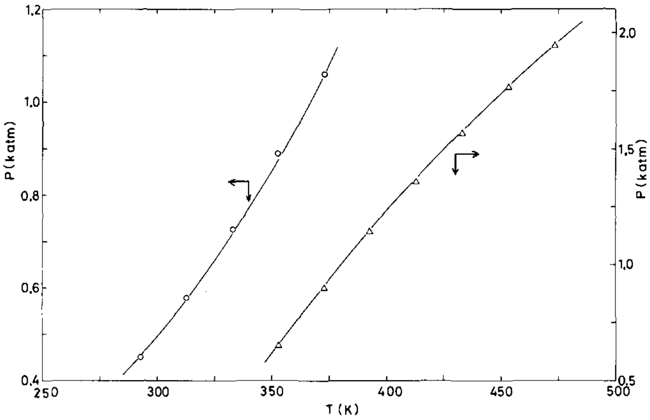

Figure 1 Pressure *versus* temperature at constant volume for: ○, PMMA (0.835 cm³ g⁻¹); △, PNBMA (0.95 cm³ g⁻¹). Data are taken from Reference 19

DISCUSSION

It is interesting to examine whether the experimental behaviour of γ_v, C_v and $\gamma_v T - P$ over a wide range of temperature and volume are explained by the equation

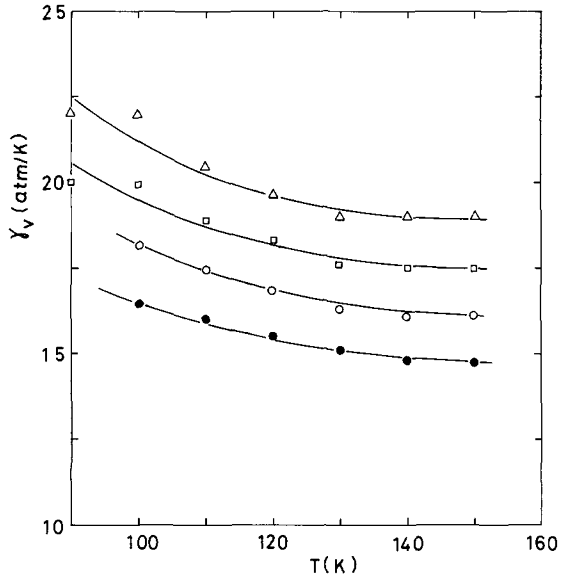

Figure 2 Thermal pressure coefficient γ_v *versus* temperature for argon at various volumes: △, 27.78; □, 28.57; ○, 29.41; ●, 30.30 cm³ mol⁻¹. Data are taken from Reference 21. ———, Calculated from equation (27)

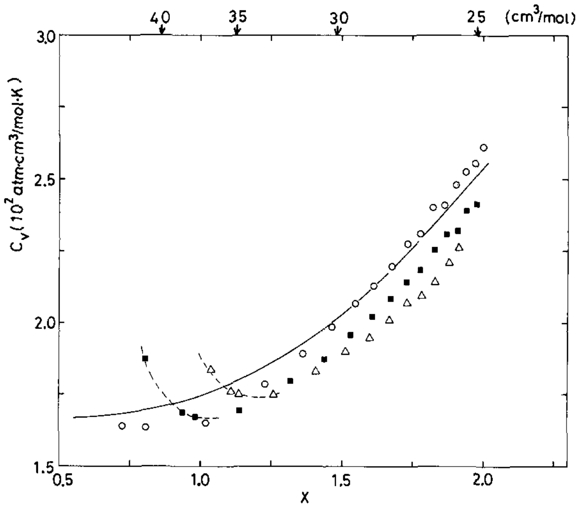

Figure 3 C_v *versus* X $(=(V_c - V)/V)$ or V for argon at various temperatures: ○, 150; ■, 140; △, 130 K. ———, Calculated from equation (29) with $n = 3.6$, $c = 0.05$ and $C_{v,0} = 1.63$. Data are from Reference 21

Table 1 Values of constants in $P = A_0 T^{k_0} + B_0$ for polymers at various constant volumes[a]

PNBMA				PS				PMMA			
V (cm³ g⁻¹)	$10^{-4}A_0$	$10^{-4}B_0$	k_0	V (cm³ g⁻¹)	$10^{-2}A_0$	$10^{-2}B_0$	k_0	V (cm³ g⁻¹)	$10^{5}A_0$	$10^{-2}B_0$	k_0
0.95	−9.42	1.51	−0.32	0.971	−9.25	1.20	−0.35	0.820	0.2	8.18	3.38
0.96	−7.23	3.42	−0.13	0.980	−11.3	8.73	−0.04	0.825	4.3	3.94	2.89
0.97	-0.10_5	7.66	-0.05_5	0.990	−8.16	1.15	−0.33	0.830	6.1	0.78	2.84
0.98	−7.30	4.06	−0.10	1.00	−7.87	1.20	−0.32	0.835	21.8	−2.45	2.60
0.99	−8.65	1.24	−0.33					0.840	61.0	−5.42	2.47
1.00	−6.80	1.54	−0.25								

[a] Data are taken from Reference 19 for PNBMA and PMMA and Reference 20 for PS. The unit of P is atm

Table 2 Constants in $\tilde{\gamma}_v = A_1\{(T_c - T)/T\}^{\delta_0} + B_1$ (equation (27)) and $\tilde{\gamma}_vT - \tilde{P} = A_2\{(T_c - T)/T\}^{\varepsilon_0} + B_2$ (equation (32)) for argon[a]

	$\tilde{\gamma}_v$			$\tilde{\gamma}_vT - \tilde{P}$			
V (cm^3 mol^{-1})	A_1	δ_0	B_1	V (cm^3 mol^{-1})	A_2	ε_0	B_2
27.03	15.5	2.23	18.6	27.0	1607	1.81	1127
27.78	7.43	1.74	17.1	28.0	1183	1.56	1198
28.57	5.26	1.43	15.7	29.0	879	1.29	1208
29.41	4.99	1.32	14.3	30.0	1071	1.62	1225
30.30	3.82	1.25	13.0	32.0	710	1.30	1134
31.25	5.05	1.54	11.7				
32.26	4.12	1.43	10.5				

[a] Data are taken from Reference 21. The units of $\tilde{\gamma}_v$ and $\tilde{P}$ are atm K^{-1} and atm, respectively

of state in this work. First, it is necessary to determine $C_2(T)$ in equation (14) based on experimental data for γ_v. We assume that $C_2(T)$ is expressed by a homogeneous function of $(T_c - T)/T$:

$$C_2(T) \sim \tilde{\gamma}_v = A_1\{(T_c - T)/T\}^{\delta_0} + B_1 \quad V = \text{const.} \quad (27)$$

Values of δ_0 determined by best fitting to data in *Figure 2* are listed in *Table 2*. C_v is given by using equations (25) and (27) as

$$C_v \sim C_v(T) - A_1(T_c/T)\alpha_0\delta_0\{(T_c - T)/T\}^{\delta_0 - 1}\exp(\alpha_0^{-1}I_0) \quad (28)$$

The divergence of C_v near T_c is due to $C_v(T)$ since $\delta_0 > 1$. If an approximation $I_0 = \int_{V_c}^{V} X^{\beta_0}/V\, \mathrm{d}V \approx -X^n$ is used, C_v in equation (28) is expressed by using $A_1(T_c/T)\alpha_0 \times \delta_0 Y^{\delta_0 - 1} = A_0(T)$ as

$$C_v = C_{v,0} + A_0(T)\{1 - \exp(-cX^n)\} \quad (29)$$

where $C_{v,0}$ is the value of C_v at $X = 0$ and $C_{v,0} = C_v(T) - A_0(T)$. A comparison between the experimental data C_v for Ar and C_v calculated by equation (29) with $n = 3.6$ and $c = 0.05$ is shown in *Figure 3*, where reasonable agreement is obtained.

Values of $\tilde{\gamma}_vT - \tilde{P}$ calculated from equation (13) using the experimental data on $\tilde{\gamma}_v$ for Ar at constant temperature are plotted against volume in *Figure 4*. $C_1(T)$ is calculated from equation (19) by

$$C_1(T) = \exp\{(\alpha_0^{-1} - a_0^{-1})I_0\}\int_{T_c}^{T} T\{\mathrm{d}C_2(T)/\mathrm{d}T\}\,\mathrm{d}T \quad (30)$$

$$\sim \exp\{(\alpha_0^{-1} - a_0^{-1})I_0\}\int_{0}^{Y} Y^{\delta_0 - 1}/(1 + Y)\,\mathrm{d}Y \quad (31)$$

where equation (27) for $C_2(T)$ and $Y = (T_c - T)/T$ are used in deriving equation (31). The function $C_1(T)$ is determined by a plot of $\tilde{\gamma}_vT - \tilde{P}$ against temperature at constant volume using the data in *Figure 4* and is expressed as

$$C_1(T) \sim \tilde{\gamma}_vT - \tilde{P} = A_2Y^{\varepsilon_0} + B_2 \quad (32)$$

where v = constant.

Table 2 shows that values of ε_0 are comparable with δ_0 in $C_2(T)$, which is expected from equation (31) through $C_1(T) \sim Y^{\delta_0}$ when $Y \ll 1$.

The volume dependence of $\tilde{\gamma}_v$ at constant temperature is analysed with equation (14) using the approximation that

$$I_0 = K - v_0 \ln X \quad (33)$$

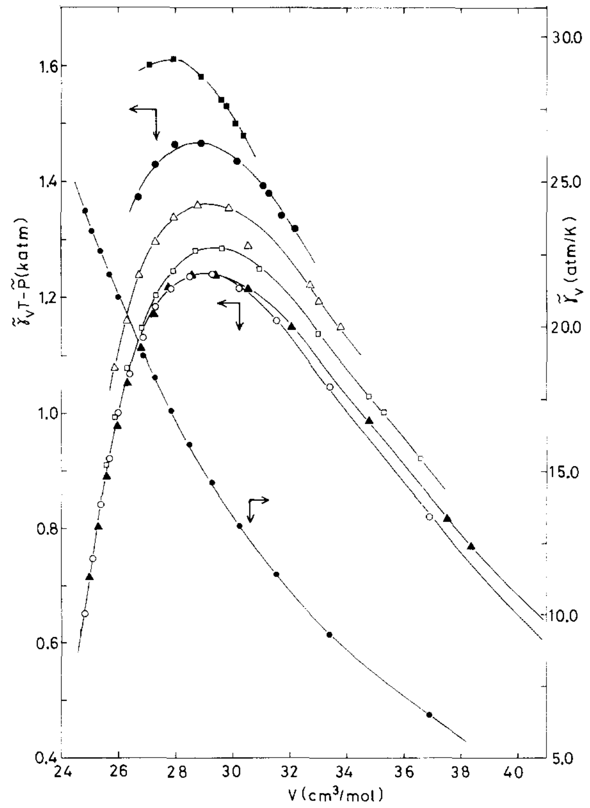

Figure 4 $\tilde{\gamma}_vT - \tilde{P}$ and $\tilde{\gamma}_v$ *versus* V for argon at various temperatures. The plots for $\tilde{\gamma}_vT - \tilde{P}$ are: ○, 150; ▲, 140; □, 130; △, 120; ●, 110; ■, 100 K. The plot for $\tilde{\gamma}_v$ is ●, 150 K. Data are taken from Reference 21

where K and v_0 are constants, which leads to

$$\tilde{\gamma}_vV = C_2^*(T)X^{(\beta_0 - v_0\alpha_0^{-1})} \quad (34)$$

As is shown in *Figure 5* a linear relation between $\ln(\tilde{\gamma}_vV)$ and $\ln X$ with a slope $(\beta_0 - v_0\alpha_0^{-1}) \leqslant 1.36$ is observed (*Table 3*). The volume dependence of $(\partial\tilde{E}/\partial V)_T = \tilde{\gamma}_vT - \tilde{P}$ for water at saturated vapour pressure calculated from the experimental data is shown in *Figure 6*, where the volume dependence of $\tilde{\gamma}_v$ is also included. In *Figure 7* an attempt is made to explain the volume dependence of $\tilde{\gamma}_vT - \tilde{P}$ by using equation (13) with $b_0 = \beta_0 = 2.60$, which is obtained experimentally from the volume dependence of α_p in equation (18) (see below). It is noteworthy that the functions $(\tilde{\gamma}_vT - \tilde{P})V$ for argon and water are almost the same in reduced form, $\ln(\tilde{\gamma}_vT - \tilde{P})V = 12.15 + 2.60\ln X - 1.8X$ for Ar and $\ln(\tilde{\gamma}_vT - \tilde{P})V = 13.21 + 2.60\ln X - 1.68X$ for water, and that a good prediction is obtained except for large X or smaller volume

Table 3 Constants in $(\alpha_p T)^{-1} = (a_0^{-1} - \alpha_0^{-1})X^{\beta_0}$ (equation (18)) and $\tilde{\gamma}_v V = C_2^* X^{(\beta_0 - \gamma_0 \alpha_0^{-1})}$ (equation (34)) for argon[a]

	$(\alpha_p T)^{-1}$		$\tilde{\gamma}_v V$		
P (atm)	$(a_0^{-1} - \alpha_0^{-1})$	β_0	T (K)	C_2^* (atm cm^3 K^{-1} mol^{-1})	$(\beta_0 - \gamma_0 \alpha_0^{-1})$
40	0.74	2.6	110	262	1.30
80	0.80	2.5	120	247	1.33
200	0.94	2.2	130	245	1.30
600	1.09	2.1	150	233	1.36

[a] Data are taken from Reference 21

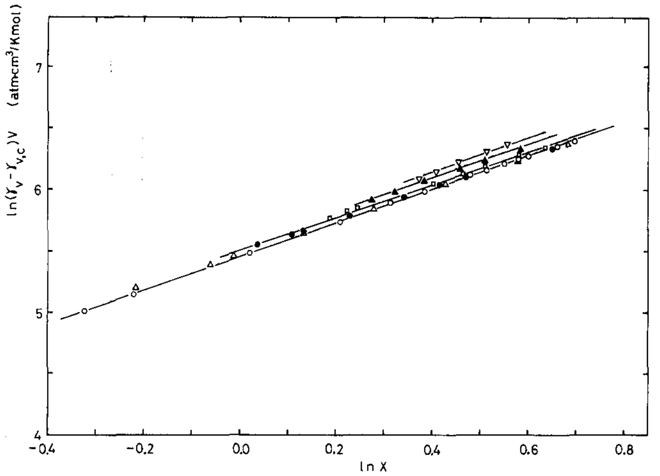

Figure 5 $\ln(\gamma_v - \gamma_{v,c})V$ *versus* $\ln X$ for argon at various temperatures: ○, 150; △, 140; ●, 130; □, 120; ▲, 110; ▽, 100 K

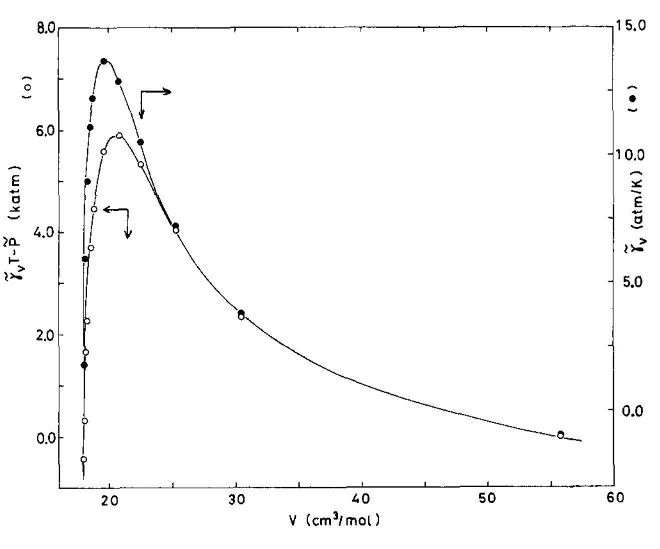

Figure 6 $\tilde{\gamma}_v T - \tilde{P}$ and $\tilde{\gamma}_v$ *versus* V plots for water at saturated vapour pressure: ○, $\tilde{\gamma}_v T - \tilde{P}$; ●, $\tilde{\gamma}_v$. Data are taken from Reference 22

corresponding to high pressure. The maximum point in the $(\tilde{\gamma}_v T - \tilde{P})$ *versus* V curve indicates an inflection point in the E–V or E–r curve. The volume at the inflection point is about 29 cm^3 mol^{-1} for Ar and 20 cm^3 mol^{-1} for water and a great difference between Ar and water is observed in the maximum internal pressure. $(\partial E/\partial V)_{T,\max} \approx 1.4$ katm for Ar and 6.0 katm for water. There is another important relation between $\tilde{\gamma}_v$–V and $(\tilde{\gamma}_v T - \tilde{P})$–$V$ curves for Ar: $\tilde{\gamma}_v$ decreases monotonously with volume from 24 to 44 cm^3 mol^{-1}, while $\tilde{\gamma}_v T - \tilde{P}$ has a maximum around 29 cm^3 mol^{-1}, which suggests that the inflection point in the E–V curve does not coincide with that in the S–V curve and that the inflection point for the entropy may exist at much smaller volume. On the other hand, if it is assumed that $\tilde{\gamma}_v$ for water depends on volume only, a maximum point for the $\tilde{\gamma}_v$–V curve is at 20 cm^3 mol^{-1}, which is the same as the maximum point in the $(\tilde{\gamma}_v T - \tilde{P})$–$V$ curve (see *Figure 6*).

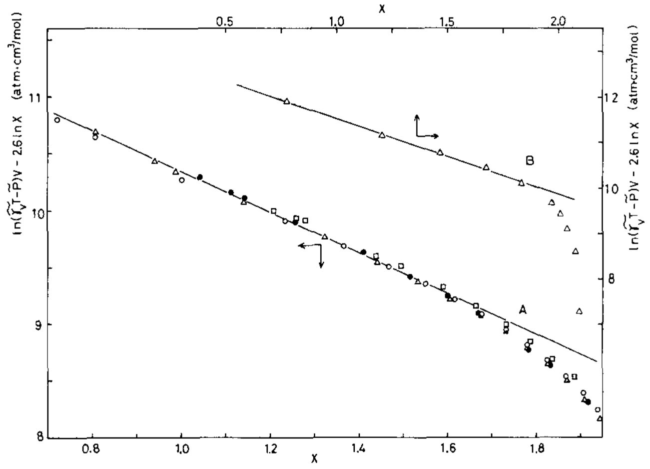

Figure 7 $\ln(\tilde{\gamma}_v T - \tilde{P})V - 2.6 \ln X$ *versus* X for argon (A) and water (B). Temperatures for argon are: ○, 150; △, 140; ●, 130; □, 120 K. Data are taken from Reference 21 for argon and Reference 22 for water at saturated vapour pressure

It is interesting to discuss the functional difference between $\tilde{\gamma}_v$ and $\tilde{\gamma}_v T - \tilde{P}$ with respect to volume at constant temperature based on equations (13) and (14) with $b_0 = \beta_0$, where the main difference appears in the constants α_0 and a_0 only. It is possible to calculate the condition for the maximum for $\tilde{\gamma}_v$ and $\tilde{\gamma}_v T - \tilde{P}$ against V, given by

$$(\partial \tilde{\gamma}_v / \partial V)_T = X^{\beta_0 + 1} - \alpha_0(1 + \beta_0)X - \alpha_0 \beta_0 = 0 \quad (35)$$

and

$$\{\partial(\tilde{\gamma}_v T - \tilde{P})/\partial V\}_T = X^{\beta_0 + 1} - a_0(1 + \beta_0)X - a_0 \beta_0 = 0 \quad (36)$$

In the simple case of $\beta_0 = 2.0$, the relation between the maximum volume for the $\tilde{\gamma}_v$–V curve and α_0 is shown in *Figure 8* (the same relation holds for a_0). The volume at the maximum point for $\tilde{\gamma}_v$ or $\tilde{\gamma}_v T - \tilde{P}$ decreases with increasing α_0 or a_0. The value of a_0 for Ar is evaluated from equation (36) with $\beta_0 = 2.60$, $X_{\max} = (V_c/V_{\max}) - 1$, $V_c = 74.6$ cm^3 mol^{-1} and $V_{\max} = 29$ cm^3 mol^{-1}, which gives $a_0 = 0.617$. The relation $a_0^{-1} - \alpha_0^{-1} = 0.94$ obtained

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* 1 atm ≈ 10^5 N

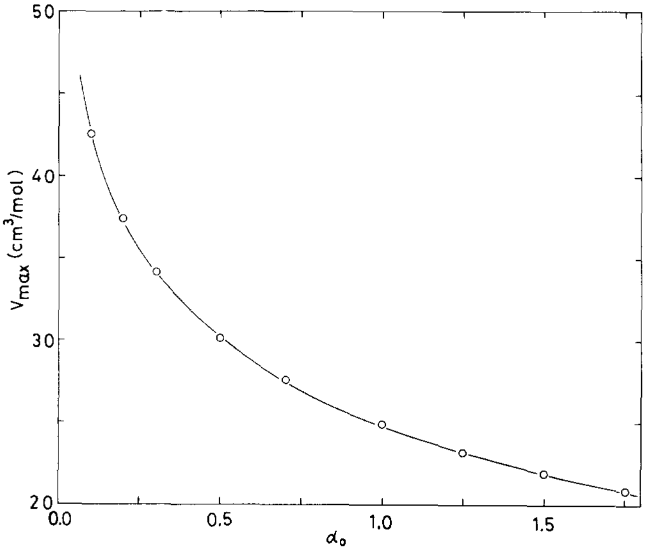

Figure 8 $V_{\max}$ *versus* α_0 calculated from equation (35) with $\beta_0=2.0$

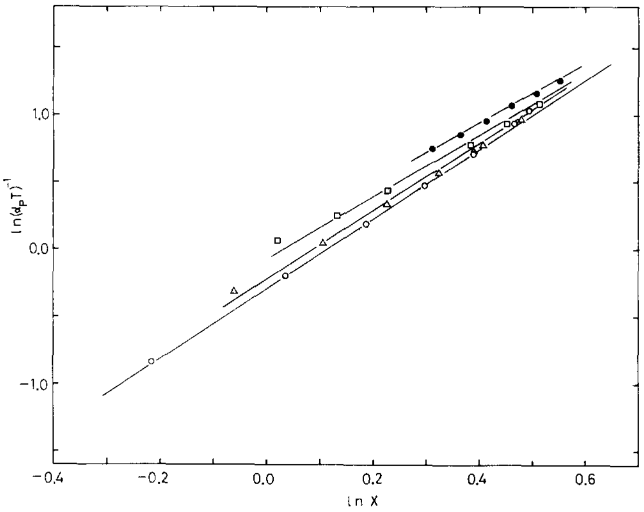

Figure 9 $\ln(\alpha_pT)^{-1}$ *versus* $\ln X$ in equation (18) for argon at various pressures: ○, 40; △, 80; □, 200; ●, 600 atm. Data are taken from Reference 21

from $(\alpha_pT)^{-1}=(a_0^{-1}-\alpha_0^{-1})X^{\beta_0}$ gives $\alpha_0=1.47$. This means the maximum volume for the $\tilde{\gamma}_v$–V curve is much smaller than that for $\tilde{\gamma}_vT-\tilde{P}$.

An examination of the expression for α_p with respect to volume is attempted in *Figure 9* based on equation (18). A linearity is observed between $\ln(\alpha_pT)^{-1}$ and $\ln X$ with a slope $2.1\leqslant\beta_0\leqslant2.6$ and $a_0^{-1}-\alpha_0^{-1}$ seems to be slightly dependent on pressure (see *Table 3*).

It is interesting to discuss an essential difference between polymers and simple liquid in terms of the equation of state. It can be obtained from *Table 1* that the temperature dependence of γ_v at constant volume is expressed by $\gamma_v\sim T^{-1.3}$ for PNBMA and PS and $\gamma_v\sim T^{1.7}$ for PMMA, approximately, where in the former case data are taken at temperatures above the glass transition temperature T_g while in the latter data are taken below T_g. The temperature dependence $\gamma_v\sim T^{-1.3}$ for the polymers is nearly the same as $\tilde{\gamma}_v\sim\{(T_c-T)/T\}^{\delta_0}$ with $1.20\leqslant\delta_0\leqslant2.23$ observed in the simple liquid Ar (see *Table 2*) because $\gamma_v\sim\{(T_c-T)/T\}^{1.3}\sim T^{-1.3}$ for a polymer with $T_c\gg T$.

For polymers, equations (8) and (9) with $X=(V_c-V)/V$ are not useful because the critical volume V_c for polymers cannot be determined experimentally. It is more practical to introduce a variable Z defined by

$$Z=(V-V_0)/V \tag{37}$$

where V_0 is the volume at the minimum point of the E–V curve. We assume that the functions $E(V,T)$ and $S(V,T)$ near the minimum point are expressed by

$$\tilde{E}=E-(\gamma_{v,0}T-P_0)(V-V_0) \tag{38}$$

$$=\tilde{E}_I'(V,T)+\tilde{E}_{II}'(T) \tag{39}$$

$$\tilde{S}=S-\gamma_{v,0}(V-V_0) \tag{40}$$

$$=\tilde{S}_I'(V,T)+\tilde{S}_{II}'(T) \tag{41}$$

where $\gamma_{v,0}$ and P_0 are values at 0 K. $\tilde{E}_I'(V,T)$ and $\tilde{S}_I'(V,T)$ are assumed to be given by

$$\tilde{E}_I'(V,T)=a_0'(\tilde{\gamma}_v'T-\tilde{P}')V\{V/(V-V_0)\}^{\lambda_0} \tag{42}$$

where $\tilde{\gamma}_v'=\gamma_v-\gamma_{v,0}=\gamma_v$ due to $\gamma_{v,0}=0$ and $\tilde{P}'=P-P_0$ and

$$\tilde{S}_I'(V,T)=\alpha_0'\tilde{\gamma}_v'V\{V/(V-V_0)\}^{\tau_0} \tag{43}$$

Following the same procedure as before, it is derived that

$$\tilde{\gamma}_v'V=C_2'(T)Z^{\tau_0}\exp(\alpha_0'^{-1}I_{z,\tau_0}) \tag{44}$$

and

$$(\tilde{\gamma}_v'T-\tilde{P}')V=C_1'(T)Z^{\lambda_0}\exp(a_0'^{-1}I_{z,\lambda_0}) \tag{45}$$

where $I_{z,x}$ is defined by

$$I_{z,x}=\int_{V\to V_0}^{V}Z^x/V\,\mathrm{d}V \qquad x=\tau_0\text{ or }\lambda_0 \tag{46a}$$

The function I_z is expressed approximately by

$$I_{z,x}=K'-\varepsilon_1\ln Z \tag{46b}$$

The thermal expansion coefficient α_p is derived under conditions that $\alpha_pT\to0$ at $V\to V_0$ as

$$(\alpha_pT)^{-1}\sim Z^{\beta_1} \qquad \beta_1<0 \tag{47}$$

Typical plots for $\ln(\alpha_pT)^{-1}$ against $\ln Z$ and $\tilde{\gamma}_v'V$ and $(\tilde{\gamma}_v'T-\tilde{P})V$ against Z are shown in *Figures 10* and *11*. Values of indices such as β_1 for polymers are listed in *Table 4*.

The function of $\tilde{E}$ around $(\partial\tilde{E}/\partial V)_T=0$ for simple liquids over a small volume is expressed by using a new

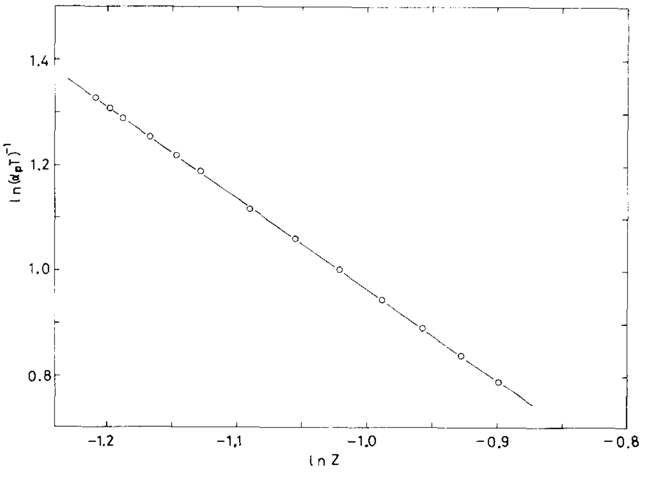

Figure 10 $\ln(\alpha_pT)^{-1}$ *versus* $\ln Z$ for polydimethyl siloxane. Data are taken from Reference 24

Table 4 Constants in $\ln(\alpha_p T)^{-1} = A_3 + \beta_1 \ln Z$ (equation (47)), $\ln(\tilde{\gamma}'_v V) = A_4 + \tau_1 \ln Z$ (equation (50)) and $\ln(\tilde{\gamma}'_v T - \tilde{P}')V = A_5 + \lambda_1 \ln Z$ (equation (51)) for various polymers[a]

Polymer[b]	$10^{-3}M_w$	V_0 (cm^3 g^{-1})	β_1	A_3	τ_1	A_4	λ_1	A_5
PIB	40.0	0.888	−1.50	−0.725	−1.64	−0.246	−0.32	7.68
PS	51.0	0.760	−1.37	−0.522	−1.89	−0.616	−0.55	7.33
PDMS	~100	0.720	−1.76	−0.800	−2.67	−1.13	−1.12	6.42

[a] $Z = (V - V_0)/V$, $\tau_1 = \tau_0 - \alpha_0^{-1}\varepsilon_1$, $\lambda_1 = \lambda_0 - a_0^{-1}\varepsilon_1$, $\tilde{\gamma}'_v = \gamma_v$ and $\tilde{P} = P$

[b] Data are taken from Reference 25 for PS, Reference 26 for PIB and Reference 24 for PDMS

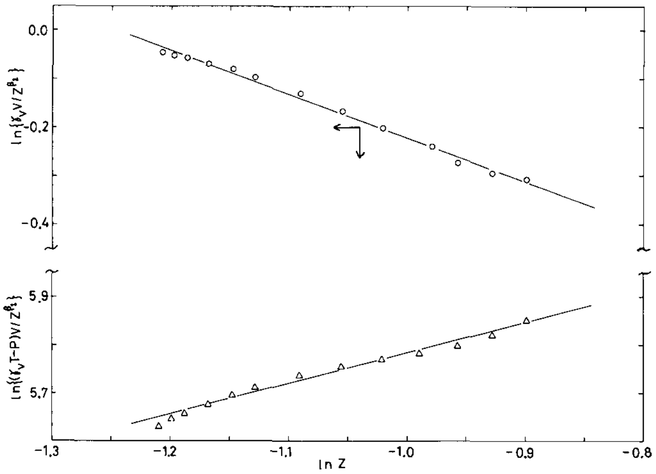

Figure 11 $\ln\{(\gamma_v T - P)V/Z^{\beta_1}\}$ *versus* $\ln Z$ and $\ln(\gamma_v V/Z^{\beta_1})$ *versus* $\ln Z$ plots for polydimethyl siloxane with $\beta_1 = -1.76$, $\gamma_{v,0} = 0$ and $P_0 = 0$ in equations (50) and (51), where $\tilde{\gamma}'_v T - \tilde{P}' = \gamma_v T - P$ and $\tilde{\gamma}'_v = \gamma_v$. Data are taken from Reference 24

variable Z defined in equation (37). The function $\tilde{\gamma}'_v T - \tilde{P}'$ around the minimum of E is given for simple liquids by $(\tilde{\gamma}'_v T - \tilde{P}')V \sim Z^{0.45}$ for water and $(\tilde{\gamma}'_v T - \tilde{P}')V \sim Z^{0.47}$ for Ar, these expressions are determined by experimental data on γ_v and $V_0 = 18.02$ cm^3 mol^{-1} for water, $V_0 = 24.2$ cm^3 mol^{-1} for Ar. It is stressed that the volume dependence of $\tilde{\gamma}_v T - \tilde{P}$ with a maximum in *Figure 4* is a general feature for all liquids, including polymers, and is explained by using two variables such as X and Z. X is useful over a liquid-like region and expresses the number of molecules of volume V around a certain molecule within the volume V_c due to $X = (V_c - V)/V$, while Z is a measure of free volume per unit volume in equation (37).

The equation of state for the liquid-like region has been determined based on equations (15) and (27) for $C_2(T)$ and (31) for $C_1(T)$:

$$\tilde{P} = (X^{\beta_0}/V)\left[\left\{T(Y^{\delta_0} + C_0) - \int_0^Y Y^{\delta_0 - 1}/(1+Y)\,\mathrm{d}Y\right\} \times \exp(\alpha_0^{-1} I_0) - D_0 \exp(a_0^{-1} I_0)\right] \quad (48)$$

This equation of state takes into account the temperature dependence of γ_v at constant volume, $(\partial\gamma_v/\partial T)_v < 0$, and $(\partial C_v/\partial V)_T < 0$ and $(\partial\gamma_v/\partial V)_T < 0$ observed experimentally. On the other hand, the equation of state for the solid-like region is given by

$$\tilde{P}' = C'_2(T)(Z^{\tau_0}/V)T \exp(\alpha'^{-1}_0 I_{z,\tau_0}) - C'_1(T)(Z^{\lambda_0}/V) \exp(a'^{-1}_0 I_{z,\lambda_0}) \quad (49)$$

where $C'_2(T)$ and $C'_1(T)$ are functions of temperature. For polymers in this work $C'_2(T)$ is given by $C'_2(T) \sim T^{k_0 - 1}$, from equations (26) and (44). $C'_1(T) \sim T^{k_0 - 1}$ is obtained from equation (45) and $C'_2(T)$ through an equation similar to equation (19). It is also derived that $\tau_0 = \lambda_0$ is not a necessary condition for the equation of state for the solid-like region as it is in a liquid-like region where $b_0 = \beta_0$. The expressions for $\tilde{\gamma}'_v V$ and $(\tilde{\gamma}'_v T - \tilde{P}')V$ simplified by equation (46b) and the above relations are given by

$$\tilde{\gamma}'_v V \sim T^{k_0 - 1} Z^{(\tau_0 - \varepsilon_1 \alpha_0^{-1})} \sim T^{k_0 - 1} Z^{\tau_1} \quad (50)$$

and

$$(\tilde{\gamma}'_v T - \tilde{P}')V \sim T^{k_0 - 1} Z^{(\lambda_0 - \varepsilon_1 a_0{}^{-1})} \sim T^{k_0 - 1} Z^{\lambda_1} \quad (51)$$

Values of indices in equations (50) and (51) are shown in *Table 4*, where values of both $\tau_0 - \varepsilon_1 \alpha_0^{-1}$ in the expression for $\tilde{\gamma}'_v V$ and $\lambda_0 - \varepsilon_1 a_0^{-1}$ in the expression for $\tilde{\gamma}'_v T - \tilde{P}'$ are negative.

Foulkes[16] derived a generalized equation of state using the Lagrange method of indeterminate multipliers which satisfies the third law of thermodynamics that $\lim_{T\to 0} S = 0$ and $\lim_{T\to 0} C_v = \lim_{T\to 0} \gamma_v = \lim_{T\to 0} \alpha_p = 0$. It is given by

$$V = (T/P)\varphi(P/T^{n+1}) + h(P) \quad (52)$$

On the other hand, Yang *et al.*[23] discussed the divergence of C_v at the critical point using the equation

$$C_v = VT(\partial^2 P/\partial T^2)_v - NT(\partial^2 \mu/\partial T^2)_v \quad (53)$$

where μ is the chemical potential $\mu = G/N$ and N is the number of molecules. In the present work it is shown that $\gamma_v \sim \{(T_c - T)/T\}^{\delta_0}$ with $\delta_0 > 1.0$ and, therefore, $(\partial\gamma_v/\partial T)_v \to 0$ in the limit $T \to T_c$ over the volume range much smaller than V_c (see *Figure 2*). It is suggested from this work that the divergence of C_v at T_c is attributed to $-NT(\partial^2\mu/\partial T^2)_v$ in equation (53) or $C_v(T)$ in equation (25). The other interesting behaviour is shown in *Figure 3* by dashed lines, where C_v increases with increasing volume over a range of larger volume, which cannot be explained by equation (25) in this work.

REFERENCES

1 Van der Waals, J. D. and Kohnstamm, P. 'Lehrbuch der Thermodynamik', Vols 1 and 2, Leipzig, Amsterdam, 1908

2 Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3507

3 Prigogine, I., Bellemans, A. and Naar-Colin, C. *J. Chem. Phys.* 1952, **26**, 751

4 Simha, R. and Somcynsky, T. *Macromolecules* 1969, **2**, 342

5 Patterson, D., Bhattacharyyra, S. N. and Picker, P. *Trans. Faraday Soc.* 1968, **64**, 648

6 Sanchez, I. C. and Lacombe, R. H. *Macromolecules* 1978, **11**, 1145

7 Fujisawa, K., Shiomi, T., Hamada, F. and Nakajima, A. *Polym. J.* 1981, **13**, 993

8 Dee, G. T. and Walsh, D. J. *Macromolecules* 1988, **21**, 811, 815

9 Saeki, S. and Yamaguchi, T. *Polymer* 1987, **28**, 484

10 Saeki, S., Tsubokawa, M. and Yamaguchi, T. *Polymer* 1988, **29**, 123

11 Bridgman, P. W. *Proc. Am. Acad. Arts Sci.* 1931, **66**, 185

12 Gibson, R. E. and Kincaid, J. F. *J. Am. Chem. Soc.* 1938, **60**, 511

13 Gibson, R. E. and Loeffler, O. H. *J. Am. Chem. Soc.* 1939, **61**, 2515

14 Gibson, R. E. and Loeffler, O. H. *J. Am. Chem. Soc.* 1941, **63**, 898

15 Scott, E. Wood, Sandus, O. and Weissman, S. *J. Am. Chem. Soc.* 1957, **79**, 1777

16 Foulkes, P. *Physica* 1951, **17**, 943

17 Saeki, S., Tsubokawa, M. and Yamaguchi, T. *Polymer* 1989, **30**, 672

18 Saeki, S., Tsubokawa, M. and Yamaguchi, T. *Polymer* 1989, **30**, 156

19 Olabisi, O. and Simha, R. *Macromolecules* 1975, **8**, 206

20 Hellwege, K. H., Knappe, W. and Lehmann, P. *Kolloid-Z. Z. Polym.* 1962, **183**, 110

21 Streett, W. B. *Physica* 1974, **76**, 59

22 Rowlinson, J. S. and Swinton, F. L. 'Liquids and Liquid Mixtures', Butterworth Scientific, London, 1982

23 Yang, C. N. and Yang, C. P. *Phys. Rev. Lett.* 1964, **13**, 303

24 Shih, H. and Flory, P. J. *Macromolecules* 1972, **5**, 758

25 Hocker, H., Blake, G. J. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2251

26 Flory, P. J., Ellenson, J. L. and Eichinger, B. E. *Macromolecules* 1968, **1**, 279