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Investigation of melting phenomenon and thermodynamic behaviour in crystalline polymers

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The simple P–V relation $V_x(P,T) = V_x(P_0,T)/\{A_x(T)[P + P_x(T)]^{mx}\}$ and T–V relation $\ln(T/T_0) = CZ^{nx}$, where $T_0 = 1$ K, $T \geqq 1$ K, $Z = \{V_x(P,T) - V(P,1)\}/V_x(P,T)$ derived in previous works have been used to calculate the compressibility and thermal expansion coefficient for crystalline polymers based on *PVT* data determined by Zoller *et al.*, Simha *et al.* and others The subscript x means a state of material such as $x = c$ for the crystalline state and $x = m$ for the melt state, m_x and n_x are constants, and $A_x(T)$ and $P_x(T)$ are the functions of temperature. The $V_x(P_0,T)$ is the specific volume at constant pressure P_0 and temperature T, and $V(P,1)$ is the specific volume at pressure P and 1 K. The average values of m_x calculated for 20 crystalline polymers are $\bar{m}_c = 0.0892$ with standard deviation $\sigma = 0.024$ in the crystalline state and $\bar{m}_m = 0.1005$ with $\sigma = 0.013$ in the melt state. The average values of n_x determined for the polymers are $\bar{n}_c = 0.0443$ with $\sigma = 0.020$ in the crystalline state and $\bar{n}_m = 0.1798$ with $\sigma = 0.017$ in the melt state. The $P_x(T)$ is continuous at melting temperature T_m and changes from a quick decreasing function below T_m to a slow decreasing one above T_m for most of the crystalline polymers used in this work except for polyethylene oxide and polyoxymethylene, which show a discontinuous change at T_m and transform from a quick decreasing function below T_m to a quick decreasing one above T_m. The quantity Z is defined as the free volume fraction, and increases with increasing temperature below and above T_m. The values of $Z_c = \{V_c(T_m) - V(1)\}/V_c(T_m)$ are in the range of 0.1073 ± 0.02, where $V_c(T_m)$ is V at T_m in the crystalline state, and $Z_m = \{V_m(T_m) - V(1)\}/V_m(T_m)$ are in the range of 0.1719 ± 0.02, where $V_m(T_m)$ is V at T_m in the melt state. The melting phenomena in crystalline polymers have been discussed based on the behaviour of $P_x(T)$ and Z over the temperature range including the melting point.

(Keywords: melting phenomenon; thermodynamic behaviour; crystalline polymer)

Nomenclature

PET	poly(ethylene terephthalate)
PP	polypropylene
NY	nylon-66
PBT	poly(butylene terephthalate)
PEEK	poly(ether ether ketone)
PEO	poly(ethylene oxide)
POM	polyoxymethylene
BPE	branched polyethylene
LPE	linear polyethylene
HMLPE	high molecular weight linear polyethylene

INTRODUCTION

The thermodynamic coefficients such as thermal expansion coefficient α_P, compressibility β_T, and thermal pressure coefficient γ_V are important quantities in characterizing the thermodynamic properties of polymeric materials and predicting the compatibility between polymers. The thermodynamic coefficients such as γ_V and α_P, and specific volume are used to evaluate the characteristic parameters V^*, T^* and P^* in the reduced equation of state by Flory[1] which reflect the intrinsic properties of individual polymers, and to estimate the solubility parameter δ by $m\delta^2 = T\gamma_V$ given by Allen[2], where m is about one. The change of entropy ΔS and internal energy ΔU can also be evaluated by $\Delta S = \int \gamma_V \, dV$ and $\Delta U = \int (\gamma_V T - P) \, dV$. Despite the rather obvious importance of these coefficients, little work has been reported for polymeric materials over a wide temperature range including transition temperature such as melting point. These coefficients can be evaluated by using empirical polynomials[3–10], Tait equation[11–16] and other equations[17,18]. In a preceding paper[19], we have determined these quantities accurately for amorphous polymers based on the P–V and T–V relations derived in the previous works[20–23] and experimental data published by many authors. The purpose of the present work is to determine these coefficients for crystalline polymers[24–31] accurately based on the experimental data over the wide ranges of temperature including T_m, and to study the melting phenomena in crystalline polymers.

DERIVATION OF BASIC EXPRESSIONS FOR COMPRESSIBILITY AND THERMAL EXPANSION COEFFICIENT

In this work we assume in the following equations that

$$P(V,T) = aV(\partial P/\partial V)_T Z^b + g(T) \qquad (1)$$

where Z is a free volume fraction defined by

$$Z = \{V_x(P,T) - V(P,1)\}/V_x(P,T) \qquad (2)$$

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and a and b are constants, $g(T)$ is a function of temperature, and $V(P,1)$ is the volume at pressure P and 1 K. Based on equation (1), the $P-V$ relation is derived by[20–23]

$$V_x(P,T) = V_x(P_0,T)/\{A_x(T)[P+P_x(T)]^{m_x}\} \tag{3}$$

Here $V_x(P_0,T)$ is the specific volume at constant pressure P_0 such as atmospheric pressure, and temperature $T, V_x(P,T)$ is the volume at P and T, $A_x(T)$ and $P_x(T)$ are the functions of temperature, and m_x are constants. By using a similar procedure to that mentioned above and a relation that

$$T(V,P) = a_1 V(\partial T/\partial V)_p Z^{b_1} + h(P) \tag{4}$$

the $T-V$ relation is derived by[20–23]

$$\ln(T/T_0) = CZ^{n_x} \tag{5}$$

where $T_0 = 1$ K, $T \geq 1$ K and n_x is a constant. The subscript x means a state such as $x = c$ for the crystalline state and $x = m$ for the melt state. The expression for β_T and α_P can be obtained from equation (3) and equation (5), respectively:

$$\beta_T = m_x/\{P+P_x(T)\} \tag{6}$$

$$\alpha_P = \{V_x(P,T) - V(P,1)\}/\{V(P,1)n_x T \ln T\} \tag{7}$$

The thermal pressure coefficient is obtained by the following thermodynamic relation

$$\gamma_V = \alpha_P/\beta_T \tag{8}$$

The values of m_x, $A_x(T)$, $P_x(T)$, n_x, C and $V(P,1)$ in equation (3) and equation (5) have been determined based on the PVT data for various crystalline polymers. The detail procedures were given in Ref. [19].

RESULTS

The values of m_x and $P_x(T)$ determined by equation (3) for various crystalline polymers are shown in *Figures 1 and 2*, respectively, and the average values of m_x for individual crystalline polymers are given in *Table 1*, while n_x, $V(P,1)$, and C determined by equation (5) are given in *Table 2*. They are used to determine the specific volume V, free volume fraction Z, β_T, α_P and γ_V at arbitrary temperature and pressure. In *Figure 1* it is demonstrated that the values of m_x change discontinuously at T_m and the values in the melt state are slightly larger than those in the the crystalline state for each polymer (see *Table 1*). The average value of m_x in the crystalline state is $\bar{m}_c = 0.0892$ with standard deviation $\sigma = 0.024$, and that in the melt state is $\bar{m}_m = 0.1005$ with $\sigma = 0.013$. The difference between the $\bar{m}_c$ and $\bar{m}_m$ indicates the Gibbs free energy function with respect to pressure $G = \int V\,dP$ above T_m differs from that below T_m, which is consistent with the behaviour of the first-order phase transition defined by Ehrenfest. *Figure 2* indicates that the function $P_x(T)$ is continuous and transforms from a quick decreasing function to a slow decreasing one at T_m for most of the polymers except for PEO and POM, where the $P_x(T)$ is discontinuous at T_m and transforms from a quick decreasing function to a quick decreasing one. The free volume fraction Z is determined by equation (2) and equation (5) based on the PVT data, and the temperature dependence of Z for various crystalline polymers is shown in *Figure 3*, where it is demonstrated that Z changes discontinuously at T_m and increases with increasing temperature below and above T_m. Values of Z below T_m tend to converge at T_m except for NY and LPE, while the $Z-T$ lines above T_m are parallel approximately. The linear dependence of $\alpha_P T$ on volume for various crystalline polymers below and above T_m is shown in *Figure 4*, which can be expressed by

$$\alpha_P T = h_1 + k_1 V \tag{9}$$

where h_1 and k_1 are constants and are given in *Table 3*. The linear relation can be expected from equation (7) that

$$\alpha_P T = \frac{-1}{n_x \ln T} + \frac{V_x(P,T)}{V(P,1)n_x \ln T}$$

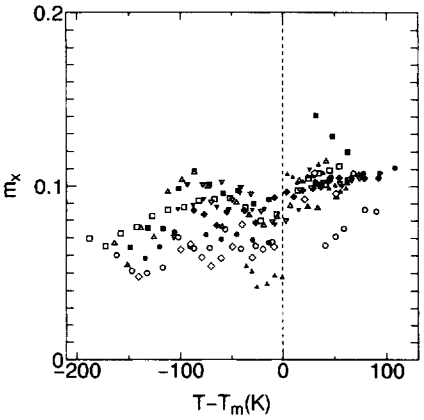

Figure 1 Temperature dependence of m_x in equation (3) for 10 pairs of polymer crystals and liquids: ○, PET; ●, PP; □, NY; ■, PBT; △, PEEK; ▲, PEO; ◇, POM; ◆, BPE; ▽, LPE; ▼, HMLPE

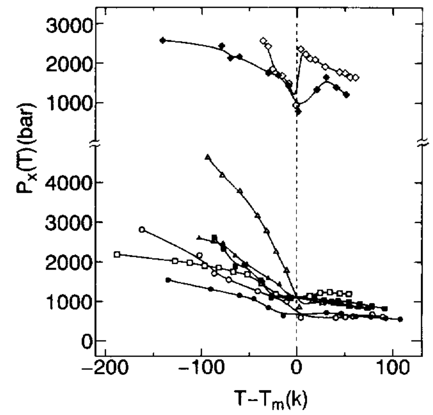

Figure 2 Temperature dependence of $P_x(T)$ in equation (3): ○, PET; ●, PP; □, NY; ■, BPE; △, LPE; ▲, HMLPE; ◇, PEO; ◆, POM

Table 1 Average values of m_x for individual crystalline polymers[a]

Polymer	PET	PP	NY	PBT	PEEK	PEO	POM	BPE	LPE	HMLPE
$\bar{m}_c$	0.0623	0.0680	0.0822	0.0900	0.0856	0.0501	0.0798	0.0859	0.0920	0.0867
$\bar{m}_m$	0.0855	0.1063	0.1062	0.1200	0.0988	0.1032	0.0994	0.1015	0.0996	0.1015

[a] The data for both m_c and m_m are available for these crystalline polymers. Either m_c or m_m is only available for the other polymers and the values of them for the polymers are not given here

Table 2 Constants and indices in equation (5) for polymers at constant pressure[a]

Polymer	Pressure (bar)	n_x	C	$V(P,1)$ ($\mathrm{cm^3\,g^{-1}}$)	Temperature range (K)	State[b]	Ref.
PP	0	0.0445	6.7207	1.0793	298.2–403.1	c	24
		0.7744	8.7062	0.4804	464.0–540.5	m	
	500	0.0580	7.0269	1.0591	298.2–418.7	c	
		0.5317	9.4252	0.6936	464.0–540.5	m	
	1000	0.0561	7.0951	1.0530	298.2–418.7	c	
		0.2375	8.7147	0.9327	464.0–540.5	m	
	1500	0.0508	7.0789	1.0484	298.2–418.7	c	
		0.4310	10.0187	0.8001	464.0–540.5	m	
	2000	0.0405	6.9316	1.0456	298.2–418.7	c	
Nylon 66	0	0.0546	6.9677	0.8542	342.0–478.0	c	24
		0.0202	6.7427	1.0057	543.8–584.3	m	
PET	0	0.0477	7.0429	0.7009	296.3–342.7	g	24
		0.0475	6.9577	0.6974	358.4–494.0	c	
		0.0341	6.8946	0.7964	550.5–610.4	m	
PBT	0	0.0329	6.5731	0.7468	302.8–333.7	g	25
		0.0498	6.8841	0.7396	347.8–483.1	c	
		0.0319	6.8489	0.8487	515.1–574.9	m	
PEEK	0	0.0857	7.9559	0.7502	304.0–420.8	g	26
		0.0916	7.6405	0.7212	431.8–562.9	c	
		0.0326	7.0013	0.8359	619.9–669.0	m	
PEO	0	0.0096	6.0156	0.8288	303.8–324.0	c	27
		0.1980	7.9356	0.7239	343.6–400.5	m	
POM	0	0.0454	6.8006	0.6929	303.0–424.2	c	28
		0.0377	6.7874	0.7918	464.7–495.0	m	
BPE	1	0.0237	6.2634	1.0550	292.3–371.1	c	29
		1.9000	9.7017	0.2826	398.3–471.2	m	
LPE	1	0.0383	6.6372	1.0036	292.7–377.7	c	29
		0.0856	7.1625	1.0995	415.3–472.9	m	
HMLPE	1	0.0379	6.5122	1.0495	291.9–376.6	c	29
		0.4133	8.2104	0.6735	409.9–472.7	m	

[a] Values of n_x, $V(P,1)$ and C have been determined for 20 crystalline polymers at various pressures, but only parts of them are given here to save space. The accuracy of specific volume determined by these parameters is in the range of 0.0000–0.0004 for various crystalline polymers. We can give the data which are useful to evaluate α_P at arbitrary temperature if asked

[b] g, glass state; c, crystalline state; m, melt state

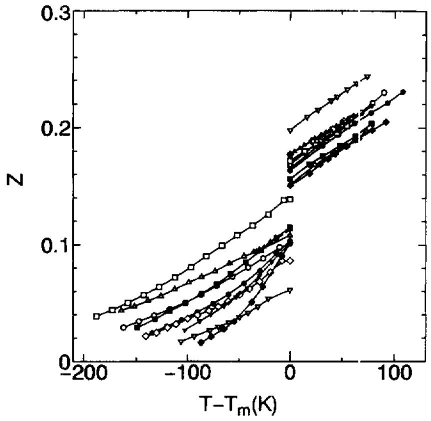

Figure 3 Temperature dependence of Z in equation (2): ○, PET; ●, PP; □, NY; ■, PBT; △, PEEK; ▲, PEO; ◇, POM; ◆, BPE; ▽, LPE; ▼, HMLPE

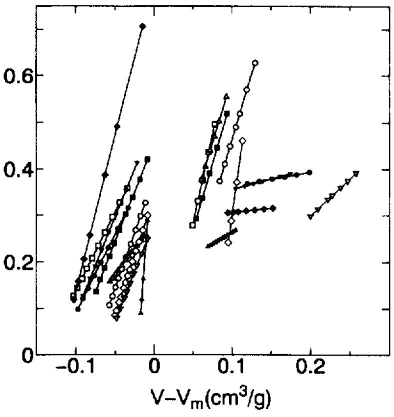

Figure 4 Volume dependence of $\alpha_P T$ for polymer crystals and liquids at atmospheric pressure: ○, PET; ●, PP; □, NY; ■, PBT; △, PEEK; ▲, PEO; ◇, POM; ◆, BPE; ▽, LPE; ▼, HMLPE

In a narrow temperature range ln T is approximately constant, therefore, $\alpha_P T$ depends on V linearly. The volume dependence of γ_V is shown in *Figure 5*, where it is observed that γ_V increases with increasing volume below T_m but decreases with increasing volume above T_m in most of the polymers.

DISCUSSION

It is interesting to discuss the free volume fraction for understanding the melting transition phenomenon. Strictly speaking, the *PVT* data used in this work are not equilibrium data, because the *PVT* data are usually determined by

Table 3 Coefficients used in equations (9), (13) and (14)

Polymer	h_1		k_1		$h_2 \times 100$	k_2	$h_3 \times 100$	k_3
	$< T_m$	$> T_m$	$< T_m$	$> T_m$				
PET	−3.2980	−0.4582	4.7422	5.6162	0.6334	0.9374	0.4072	0.9911
PP	−3.6550	−0.0465	3.3938	0.3139	2.1246	0.7356	0.5195	0.9337
NY	−2.8707	−0.6511	3.3735	7.6150	0.5647	0.9349	0.3915	0.9417
PBT	−3.1578	−0.8176	4.2853	5.6898	0.8735	0.8829	0.5072	0.9173
PEEK	−1.6041	−0.5840	2.2461	5.5000	0.3161	0.9801	0.5497	0.8800
PEO	−7.9173	−0.6816	21.6203	0.9954	0.5075	0.9840	0.4102	0.9325
POM	−3.5481	−0.8339	5.1315	11.8031	1.3974	0.8105	0.2583	1.0405
BPE	−7.0709	0.0772	6.7088	0.1800	3.9832	0.6921	0.3373	1.0434
LPE	−4.3086	−0.7539	4.2986	1.6175	1.1085	0.9016	0.4255	0.9262
HMLPE	−4.3515	−0.2371	4.1546	0.4675	2.0948	0.7737	0.4555	0.9818
Average	—	—	—	—	—	0.8633	—	0.9588

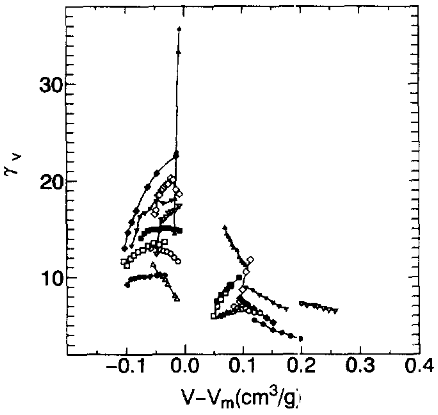

Figure 5 Volume dependence of γ_V for polymer crystals and liquids at atmospheric pressure: ○, PET; ●, PP; □, NY; ■, PBT; △, PEEK, ▲, PEO; ◇, POM; ◆, BPE, ▽, LPE; ▼, HMLPE

changing pressure with finite time under constant temperature, or by changing temperature with finite time under constant pressure, and the samples used are not perfect crystalline polymers with 100% crystallinity and infinite lamella thickness. Therefore, Z and T_m determined based on the non-equilibrium *PVT* data are also non-equilibrium values. It is shown in *Figure 3* and *Table 4* that values of $Z_c = \{V_c(T_m) - V(1)\}/V_c(T_m)$ converge to the average value of 0.1073 except for NY and LPE. One can obtain from $\bar{Z}_c = 0.1073$ that

$$V_c(T_m) = 1.120V(1) \tag{10}$$

where $V_c(T_m)$ is the volume at T_m in the crystalline state. Equation (10) indicates that when the volume expands up to 1.120 times $V(1)$ the melting phenomena will occur. In other words, the melting transition occurs when free volume fraction reaches about 10.7%, irrespective of the kind of polymer. Lindemann[32] postulated that melting occurs when the amplitude of atomic vibration has become about 10% of the distance of separation of atomic centres at 0 K, which is consistent with $V_c(T_m) = 1.120V(1)$ in this work.

The values of $Z_m = \{V_m(T_m) - V(1)\}/V_m(T_m)$ are in the range of 0.1719 ± 0.02 (see *Table 4*), which means that the free volume fraction at T_m in the melt state does not depend on the kind of polymers. If we assume $Z_m = 0.1719$, the following relation can be obtained

$$V_m(T_m) = 1.208V(1) \tag{11}$$

where $V_m(T_m)$ is the volume at T_m in the melt state. The another constant obtained using equation (10) and (11) is

$$V_{\text{ratio}} = V_m(T_m)/V_c(T_m) = 1.078 \tag{12}$$

which indicates that the volume expansion per unit volume at T_m defined by $\{V_m(T_m) - V_c(T_m)\}/V_c(T_m)$ is about 7.8% for crystalline polymers in this work. The individual values of V_{ratio} for various crystalline polymers are given in *Table 4*.

The Z–T lines are nearly parallel above T_m, and there is little difference in Z at T_m as shown in *Figure 3*. The $Z/Z_m - T$ lines will overlap to the one line while $Z/Z_c - T$ lines only converge on one point at T_m. Based on the

Table 4 Quantities determined at T_m for var ous crystalline polymers

Polymer	T_m(K)	$V_c(T_m)$(cm^3 g^{-1})	$V_m(T_m)$(cm^3 g^{-1})	$V(1)$(cm^3 g^{-1})	Z_c	Z_m	V_{ratio}
PET	520.3	0.7758	0.8390	0.6974	0.1011	0.1688	1.0815
PP	432.6	1.2036	1.2900	1.0793	0.1033	0.1633	1.0718
NY	529.7	0.9918	1.0310	0.8542	0.1387	0.1715	1.0395
PBT	496.6	0.8437	0.8850	0.7396	0.1234	0.1643	1.0490
PEEK	595.8	0.8411	0.8840	0.7212	0.1426	0.1842	1.0510
PEO	339.4	0.8502	0.9160	0.7541	0.1130	0.1767	1.0774
POM	443.5	0.7583	0.8420	0.6929	0.0862	0.1771	1.1104
BPE	379.2	1.1743	1.2420	1.0550	0.1016	0.1506	1.0577
LPE	399.0	1.0690	1.2510	1.0036	0.0612	0.1978	1.1703
HMLPE	394.5	1.1688	1.2570	1.0495	0.1021	0.1651	1.0755
average	—	—	—	—	0.1073	0.1719	1.0784

above results we proposed the following empirical V–T relations:

$$Z/Z_c = 1 - h_2(T_m - T)^{k_2} \quad T < T_m \tag{13}$$

$$Z/Z_m = 1 - h_3(T - T_m)^{k_3} \quad T > T_m \tag{14}$$

where h_2, k_2, h_3 and k_3 are constants and are given in *Table 3*. If $\bar{Z}_c = 0.1073$, $\bar{Z}_m = 0.1719$, and the average values of k_2 and k_3, namely, $\bar{k}_2 = 0.8633$ and $\bar{k}_3 = 0.9588$, are used, equation (13) and (14) can be simplified to be

$$V = \frac{V(P,1)}{0.8927 + 0.1073h_2(T_m - T)^{0.8633}} \quad T < T_m \tag{13a}$$

$$V = \frac{V(P,1)}{1 - 0.1719\{1 + h_3(T - T_m)^{0.9588}\}} \quad T > T_m \tag{14a}$$

There is only one parameter h_2 in equation (13a) and h_3 in equation (14a) if we know T_m and $V_c(T_m)$ because $V_c(T_m) = 1.120V(1)$.

It is interesting to compare the glass transition and melting transition behaviours in polymeric materials based on the simple P–V relation in this work. The average values of m_x for amorphous polymers determined in a previous work[19] are $\bar{m}_g = 0.1101$ for $T < T_g$ and $\bar{m}_l = 0.0953$ for $T > T_g$, which are compared with $\bar{m}_c = 0.0892$ for $T < T_m$ and $\bar{m}_m = 0.1005$ for $T > T_m$ for crystalline polymers in this work. Values of m_x depend on state of polymer and $\bar{m}_g > \bar{m}_m > \bar{m}_l > \bar{m}_c$. The $P_x(T)$ is almost constant below and above T_g but changes continuously and drastically in the vicinity of T_g for amorphous polymers, while $P_x(T)$ changes continuously from a quick decreasing function below T_m to almost a constant above T_m, and T_m corresponds to the transition point, at which $P_x(T)$ is about 1 kbar for various crystalline polymers. The γ_V changes continuously at T_g and has a maximum point at T_g while γ_V changes discontinuously at T_m, and increases with increasing volume or temperature below T_m but decreases with increasing volume or temperature above T_m.

CONCLUSIONS

The following conclusions are obtained in this work.

(1) The average values of m_x in the P–V relation $V_x(P,T) = V_x(P_0,T)\{A_x(T)[P + P_x(T)]^{m_x}\}$ are $\bar{m}_c = 0.0892$ for $T < T_m$ and $\bar{m}_m = 0.1005$ for $T > T_m$, which means that the Gibbs free energy function and also the *PVT* function are different below and above T_m. This behaviour around T_m is consistent with the definition of the first-order phase transition by Ehrenfest.

(2) The $P_x(T)$ function transforms from a quickly decreasing function to a slowly decreasing one at T_m for most of the crystalline polymers. The values of $P_x(T)$ at the transition point are about 1 kbar, at which the melting of crystalline polymers occurs.

(3) The free volume fraction defined by $Z = \{V_x(P,T) - V(P,1)\}/V_x(P,T)$ is determined for various crystalline polymers, and $Z_c = \{V_c(T_m) - V(1)\}/V_c(T_m)$ in the crystalline state is nearly a constant 0.1073, which means that the melting transition of crystalline polymers occurs when the free volume fraction reaches 0.1073, irrespective of the kind of polymer. The free volume fraction $Z_m = \{V_m(T_m) - V(1)\}/V_m(T_m)$ at T_m in the melt state is also a constant 0.1719.

(4) The values of $\alpha_P T$ increase linearly with increasing volume below and above T_m, but the values change discontinuously at T_m.

(5) The values of γ_V increase with increasing volume below T_m but decrease with increasing volume above T_m and change discontinuously at T_m.

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