Correlation between the equation of state and the pressure dependence of glass transition and melting temperatures in polymers and rare-gas solids

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A correlation between the equation of state and the pressure dependence of the glass transition temperature T_g in polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) and the pressure dependence of the melting temperature T_m in polymers such as polyethylene (PE), in rare-gas solids such as argon (Ar) and in hydrogen (H_2) has been examined based on the experimental data by Simha, Zoller and Rehage for polymers and Cheng, Mills and Zha for rare-gas solids and an equation of state derived in a previous work. The volume–pressure relation at constant temperature for solid and liquid states is expressed by:

$$V_x(P_0, T)/V_x(P, T) = A_x(P + P_x)^{m_x}$$

where $V_x(P_0, T)$ is the volume at constant pressure P_0 and temperature T, $V_x(P, T)$ is the volume at P and T, P_x is a function of temperature, m_x is a constant and the subscript x means a state such as $x = l$ for liquid and $x = s$ for solid. It is found that values of P_x change discontinuously with increasing temperature in the vicinity of T_g, while m_x changes discontinuously at T_m where P_x is continuous with respect to temperature. Values of $F_{m,s}$ defined by $F_{m,s} = 1 - V_s(P_m, 0)/V_s(P_m, T_m)$ for a rare-gas solid such as Ar are calculated based on the experimental data and are around 0.09 for Ar, independent of pressure, where $V_s(P_m, T_m)$ is the volume of solid phase at T_m. Values of F_g defined by $F_g = 1 - V_s(P_g, T_0)/V(P_g, T_g)$ at T_g are 0.036–0.055 for PS and 0.018–0.036 for PMMA. A three dimensional P–V–T surface over the temperature region including T_g and T_m is established based on the experimental data.

(**Keywords: equation of state; glass transition temperature; melting temperature; polymer; rare-gas solid; solid–liquid critical point; Ehrenfest equation; freezing model**)

INTRODUCTION

The phase transition temperatures of solids, such as the glass transition temperature T_g and melting temperature T_m, are very important quantities from practical and theoretical points of view. Investigations of the pressure dependence of T_g and T_m have been done in the rare-gas solids such as argon (Ar)[1–5] and in hydrogen (H_2)[6–10], helium (He)[6,11–14], nitrogen (N_2)[1,15,16] and methane[16] at high pressure above 10 kbar for (dT_m/dP), and in polymers such as polystyrene (PS)[17–19], poly(methyl methacrylate) (PMMA)[20] and others[21–24] for (dT_g/dP) and polyethylene (PE)[20,25] and others[26–28] for (dT_m/dP), where both T_m and T_g increase with increasing pressure. One interesting topic is concerned with the solid–liquid critical point, which has been examined in rare-gas solids experimentally[1,2,5,9,16,29] and theoretically[30,31]. The other point is related to the glass transition phenomena, where two models, the Ehrenfest model of second-order phase transition and the kinetic freezing model, have been examined theoretically and experimentally[18,21,24,32,33].

The main purpose of this work is to examine the correlation between the equation of state derived in the previous work and the phase transition behaviour based on the experimental data over a wide range of pressure to provide a deeper understanding of transition phenomena in polymer and rare-gas solids.

DERIVATION OF BASIC EQUATION FOR THE P–V ISOTHERM IN THE VICINITY OF T_g AND T_m

In previous work the following simple relation was derived from the homogeneous function method. In the liquid state, the relation is given by[34]:

$$\ln[V_l(P, T)/V_l(1, T)] = -A_l[P + P_l(T)]^{m_l} + B(T) \tag{1a}$$

while that in the solid state is[35]:

$$V_s(1, T)/V_s(P, T) = A_s[P + P_s(T)]^{m_s} \tag{2}$$

where $V_x(1, T)$ is the volume at atmospheric pressure and temperature T, $P_l(T)$ and $P_s(T)$ are functions of temperature, and A_l, A_s, m_l and m_s are constants. If the approximation for equation (1a) that $V(1, T)/V(P, T) = 1 + X$, $X \ll 1$, is used, the following equation is derived:

$$V_l(1, T)/V_l(P, T) = A_l[P + P_l(T)]^{m_l} \tag{1b}$$

because $B(T) = A_l(1 + P_l)^{m_l} \sim A_l P_l^{m_l}$ and $A_l P_l^{m_l} = 1.0$

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Table 1 Constants and indices in equation (3) for rare-gas solids and polymers at constant temperature

System	T (K)	m_x	P_x (bar)	$V(P_0, T)$ (cm^3 g^{-1})	P_0 (bar)	A_x	P_{max} (kbar)	Ref.
Ar	90	0.109	446	0.7252	10	0.5142	0.2	38
	100	0.119	372	0.7612	10	0.4942	0.6	38
	110	0.120	267	0.7542	200	0.4783	1.2	3
	120	0.135	232	0.7878	200	0.4409	1.6	3
	140	0.149	97	0.8706	200	0.4287	2.8	3
	160	0.159	−27	0.9900	200	0.4416	3.8	3
	180	0.165	−117	1.172	200	0.4872	5.0	3
	200	0.180	−159	1.431	200	0.5136	6.2	3
PS	310	0.0972	2310	0.9590	1	0.4710	4.0	18
	330	0.1008	2400	0.9633	1	0.4563	4.0	18
	350	0.1016	2320	0.9683	1	0.4550	4.0	18
	420	0.0956	1350	1.006	1	0.5020	4.0	18
	440	0.1253	1330	1.037	1	0.4060	4.0	18
	460	0.0988	1025	1.041	1	0.5041	4.0	18
	T_g line	0.0966	2740	0.9710	1	0.4655	4.0	18
PMMA	290.4	0.0983	3695	0.8442	1	0.4459	2.0	20
	330.0	0.1016	3135	0.8513	1	0.4386	2.0	20
	353.3	0.1016	3135	0.8566	1	0.4413	2.0	20
	374.1	0.0994	2880	0.8620	1	0.4531	2.0	20
	397.7	0.0945	1790	0.8728	1	0.4928	2.0	20
	408.3	0.0988	1770	0.8780	1	0.4774	2.0	20
	419.9	0.0992	1730	0.8838	1	0.4772	2.0	20
	432.2	0.1034	1730	0.8902	1	0.4586	2.0	20
PNBMA (poly(n-butyl methacrylate))	346.7	0.1014	1760	0.9781	1	0.4687	2.0	20
	367.7	0.1014	1545	0.9921	1	0.4749	2.0	20
	406.3	0.1030	1295	1.020	1	0.4779	2.0	20
	433.4	0.0998	1075	1.040	1	0.4985	2.0	20
	472.7	0.1036	904	1.071	1	0.4941	2.0	20
PCHMA (poly(cyclohexyl methacrylate))	291.8	0.0893	3480	0.9083	1	0.4824	2.0	20
	314.2	0.0933	3480	0.9133	1	0.4672	2.0	20
	337.2	0.0980	3400	0.9185	1	0.4507	2.0	20
	395.9	0.0875	1490	0.9394	1	0.5277	2.0	20
	407.5	0.1023	1650	0.9548	1	0.4729	2.0	20
	420.5	0.1023	1540	0.9533	1	0.4718	2.0	20
	431.4	0.0962	1340	0.9596	1	0.5003	2.0	20
	453.1	0.1018	1300	0.9727	1	0.4820	2.0	20
	472.1	0.1058	1230	0.9845	1	0.4713	2.0	20
PSF (polysulphone)	323.2	0.0966	4247	0.814	1	0.4461	2.0	21
	373.2	0.1106	3926	0.822	1	0.393	2.0	21
	423.2	0.0706	2530	0.831	1	0.575	2.0	21
	583.2	0.0984	1246	0.901	1	0.4960	2.0	21
	623.2	0.1102	1246	0.923	1	0.4559	2.0	21
Phenoxy	393.2	0.0836	1795	0.8915	1	0.5344	1.8	23
	473.2	0.0986	1590	0.9357	1	0.4835	1.8	23
	523.2	0.1004	1290	0.9679	1	0.4870	1.8	23
	573.2	0.1070	1152	1.000	1	0.4698	1.8	23
Linear PE	305.5	0.1002	4600	1.0255	1	0.4295	2.0	20
	320.8	0.1008	4170	1.0308	1	0.4317	2.0	20
	349.6	0.0924	3070	1.0429	1	0.4764	2.0	20
	377.7	0.0802	2025	1.0605	1	0.5430	2.0	20
	388.7	0.0796	1780	1.0719	1	0.5511	2.0	20
	426.1	0.1002	970	1.2787	1	0.5018	2.0	20
	438.6	0.1034	970	1.2915	1	0.4914	2.0	20
	444.3	0.1040	940	1.2970	1	0.4907	2.0	20
	454.1	0.1022	870	1.3075	1	0.5006	2.0	20
	472.9	0.1044	825	1.3271	1	0.4961	2.0	20

Table 1 (*continued*)

System	T (K)	m_x	P_x (bar)	$V(P_0, T)$ (cm^3 g^{-1})	P_0 (bar)	A_x	P_{max} (kbar)	Ref.
Branched PE	292.3	0.0845	2540	1.072	1	0.5154	2.0	20
	314.6	0.0803	2030	1.0847	1	0.5432	2.0	20
	341.7	0.082	1430	1.112	1	0.5512	2.0	20
	352.7	0.0775	1070	1.127	1	0.5824	2.0	20
	371.1	0.0965	1140	1.1595	1	0.5070	2.0	20
	382.8	0.0975	730	1.194	1	0.5261	2.0	20
	398.3	0.100	755	1.2570	1	0.5264	2.0	20
	408.3	0.0978	1010	1.2692	1	0.5083	2.0	20
	415.9	0.100	995	1.2762	1	0.5013	2.0	20
	422.7	0.1024	1000	1.2827	1	0.4930	2.0	20
	433.7	0.106	1000	1.293	1	0.4808	2.0	20
	445.2	0.1072	980	1.3037	1	0.4779	2.0	20
	471.2	0.1052	830	1.327	1	0.4933	2.0	20
High-M_w PE	291.9	0.0856	2540	1.0783	1	0.5111	2.0	20
	317.2	0.0912	2420	1.0933	1	0.4912	2.0	20
	342.0	0.0886	1990	1.1108	1	0.5102	2.0	20
	364.7	0.0892	1650	1.1326	1	0.5165	2.0	20
	386.6	0.0728	980	1.1620	1	0.6058	2.0	20
	397.7	0.0732	720	1.1900	1	0.6179	2.0	20
	430.7	0.1020	970	1.2970	1	0.4959	2.0	20
	441.1	0.1032	960	1.3084	1	0.4923	2.0	20
	461.0	0.1042	880	1.3306	1	0.4937	2.0	20
	472.7	0.1070	880	1.3435	1	0.4843	2.0	20
Low-density PE	301.2	0.0586	1427	1.095	1	0.6533	2.0	25
	323.2	0.0696	1321	1.114	1	0.6062	2.0	25
	348.2	0.120	2334	1.140	1	0.3943	2.0	25
	373.2	0.109	1520	1.180	1	0.4493	2.0	25
	423.2	0.0918	949	1.273	1	0.5319	2.0	25
	448.2	0.0986	937	1.295	1	0.5084	2.0	25
	473.2	0.1052	927	1.317	1	0.4862	2.0	25
	498.2	0.0970	734	1.338	1	0.5263	2.0	25
PP (polypropylene)	323.2	0.084	2500	1.113	1	0.5184	2.0	28
	373.2	0.067	1265	1.141	1	0.6193	2.0	28
	473.2	0.101	741	1.326	1	0.5128	2.0	28
	523.2	0.115	780	1.367	1	0.4657	2.0	28
	573.2	0.104	500	1.418	1	0.5237	2.0	28
Poly(but-1-ene)	302.9	0.059	1273	1.098	1	0.6557	2.0	28
	323.2	0.0672	1408	1.110	1	0.6143	2.0	28
	348.2	0.064	1123	1.127	1	0.6381	2.0	28
	373.2	0.0745	1141	1.146	1	0.5919	2.0	28
	423.2	0.0896	809	1.264	1	0.5487	2.0	28
	473.2	0.0893	638	1.306	1	0.5616	2.0	28
	523.2	0.0994	593	1.352	1	0.5301	2.0	28
PET (poly(ethylene terephthalate))	301.2	0.0708	4149	0.7107	1	0.5543	2.0	22
	407.2	0.0680	2697	0.7266	1	0.5846	2.0	22
	500.2	0.0624	1442	0.7520	1	0.6353	2.0	22
	566.9	0.1098	1363	0.8633	1	0.4528	2.0	22
	616.2	0.0858	814	0.8906	1	0.5626	2.0	22
Poly(4-methyl-pent-1-ene)	302.2	0.090	1795	1.2080	1	0.5095	2.0	26
	346.1	0.0966	1569	1.233	1	0.4912	2.0	26
	388.6	0.0974	1305	1.259	1	0.4974	2.0	26
	428.0	0.0936	1030	1.286	1	0.5223	2.0	26
	469.5	0.0880	721	1.321	1	0.5606	2.0	26
	490.9	0.0832	505	1.348	1	0.5956	2.0	26
	523.7	0.1048	544	1.400	1	0.5171	2.0	26
	558.8	0.1057	487	1.432	1	0.5199	2.0	26
	592.1	0.1073	407	1.474	1	0.5248	2.0	26

Table 1 (*continued*)

System	T(K)	m_x	P_x(bar)	$V(P_0, T)$ (cm^3 g^{-1})	P_0(bar)	A_x	P_{max} (kbar)	Ref.
PTFE	323.2	0.0698	1574	0.4684	1	0.5980	2.0	27
(poly(tetrafluoroethylene))	373.2	0.0796	1550	0.4784	1	0.5573	2.0	27
	403.2	0.0576	878	0.4845	1	0.6767	2.0	27
	473.2	0.0638	623	0.5029	1	0.6705	2.0	27
	553.2	0.0682	316	0.5384	1	0.6757	2.0	27
	593.2	0.0743	151	0.5790	1	0.6870	2.0	27
	643.2	0.1110	170	0.6755	1	0.5656	2.0	27

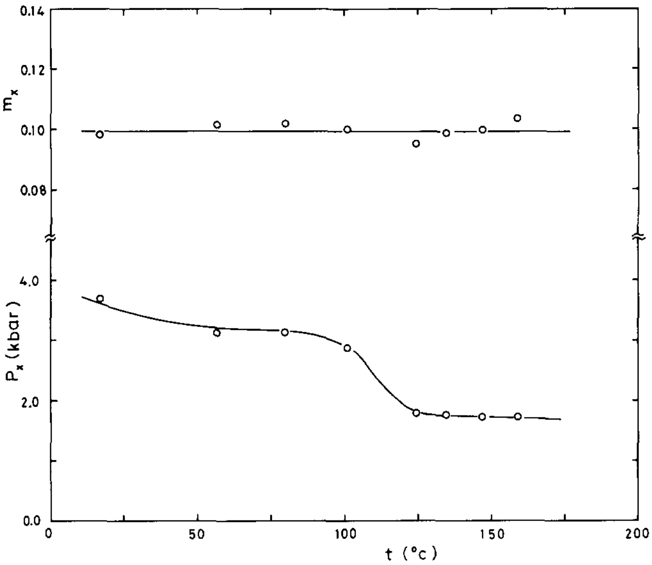

Figure 1 M_x–t and P_x–t plots for PMMA in equation (3). The data are taken from ref. 20

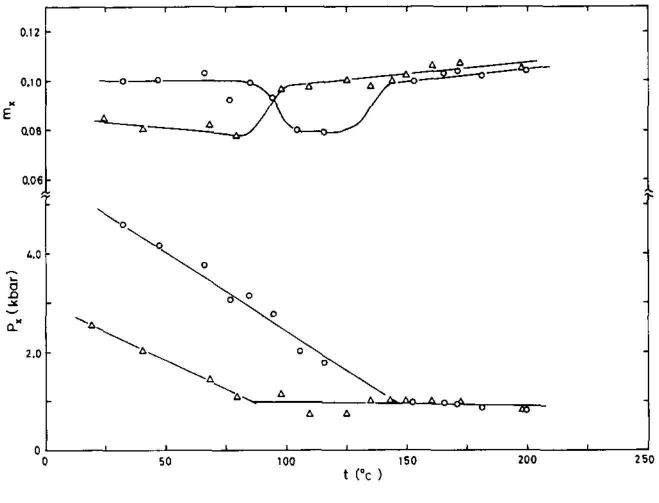

Figure 2 M_x–t and P_x–t plots for linear PE (○) and branched PE (△) in equation (3). The data are taken from ref. 20

from equation (1b) and

$$\ln V_l(1, T)/V_l(P, T) \sim V_l(1, T)/V_l(P, T) - 1,$$

which is similar to that of a solid, equation (2). Therefore, the expression of the P–V isotherm for solid and liquid states is:

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

where $x = 1$ for liquid state and $x =$ s for solid state, and P_0 is a constant pressure.

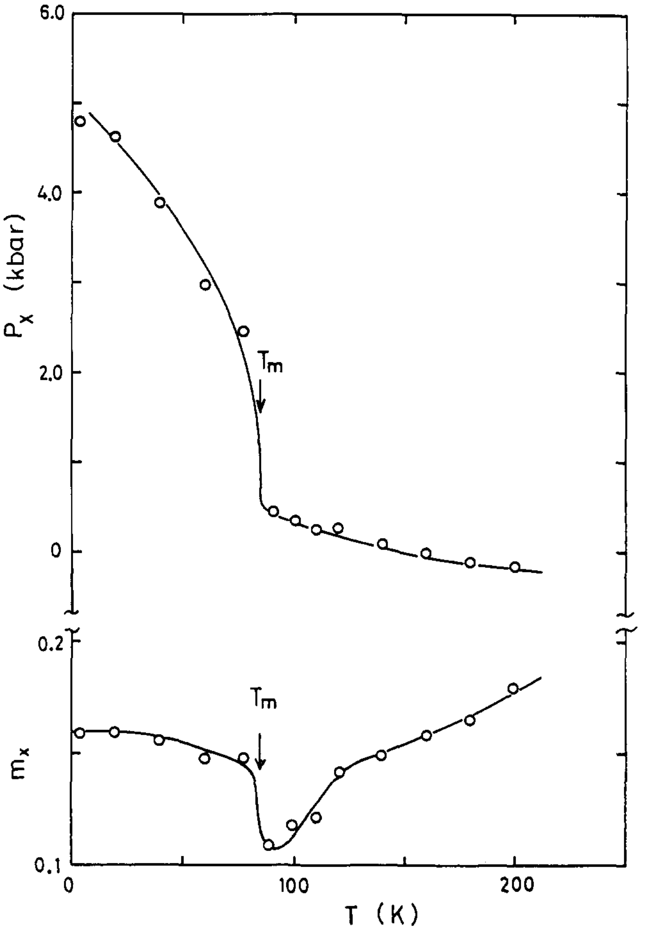

Figure 3 M_x–T and P_x–T plots for Ar in equation (3); T_m is the melting temperature. The data are taken from ref. 3 for $T \geqslant 110$ K and refs 35 and 38 for $T < 110$ K

RESULTS

The values of m_x and P_x calculated by using equation (3) for various polymers and rare-gas solids are listed in *Table 1*. The typical temperature dependence of m_x and P_x for an amorphous polymer PMMA, a crystalline polymer PE and a rare-gas solid argon (Ar) is shown in *Figures 1, 2* and *3*, where it is demonstrated that, at T_g, P_x decreases discontinuously with increasing temperature and m_x seems to be constant over T_g. On the other hand, m_x changes discontinuously at T_m and P_x decreases continuously but the slope in the P_x–T plot changes from large negative to small negative except for Ar.

It is interesting to determine the free volume fraction at the transition temperature, which is defined in this work by:

$$F_{y,x} = [V_x(P_y, T_y) - V_s(P_y, T_0)]/V_x(P_y, T_y) \quad (4)$$

Table 2 Values of $F_{y,x}$ for polymers and rare-gas solids

System	$F_{y,x}$	T_0 (K)	P_y (kbar)	y	x	$V_s(P_y, T_0)^a$ ($cm^3 g^{-1}$)	Ref.
Ar	0.0855	4.0	0.451	m	s	0.5572	3
	0.0892	4.0	1.051	m	s	0.5477	3
	0.0897	4.0	1.674	m	s	0.5389	3
	0.0871	4.0	3.805	m	s	0.5151	3
	0.0885	4.0	5.003	m	s	0.5045	3
	0.0894	4.0	6.335	m	s	0.4944	3
n-H_2	0.0584	4.0	4.733	m	s	6.824	9
	0.0515	4.0	6.378	m	s	6.417	9
	0.0613	4.0	9.010	m	s	5.964	9
	0.0535	4.0	12.527	m	s	5.554	9
	0.0488	4.0	14.626	m	s	5.369	9
	0.0585	4.0	18.710	m	s	5.086	9
PS ($M_w = 27.9 \times 10^4$, $M_w/M_n = 3.08$)	0.0409	0	0.001	g	—	0.938	17
	0.0381	0	0.600	g	–	0.921	17
	0.0360	0	1.000	g	–	0.911	17
	0.0365	0	1.600	g	–	0.897	17
	0.0390	0	2.000	g	–	0.888	17
PS ($M_w = 2.05 \times 10^3$, $M_w/M_n = 1.1$)	0.054	0	0.001	g, M_w	–	0.909	36
($M_w = 1.04 \times 10^4$)	0.0537	0	0.001	g, M_w	–	0.916	36
($M_w = 1.98 \times 10^4$)	0.0541	0	0.001	g, M_w	–	0.917	36
($M_w = 11.1 \times 10^4$)	0.0524	0	0.001	g, M_w	–	0.918	36
PMMA	0.0356	0	0.001	g	–	0.831	20
	0.0290	0	0.400	g	–	0.826	20
	0.0245	0	1.000	g	–	0.818	20
	0.0196	0	1.600	g	–	0.811	20
	0.0184	0	2.000	g	–	0.806	20
PSF	0.0551	0	0.490	g	–	0.781	21
	0.0571	0	0.981	g	–	0.771	21
	0.0607	0	1.471	g	–	0.761	21

^{a}Values of $V_s(P_y, T_0)$ for polymers are obtained using the data of V below T_g

Table 3 Values of C and n_l in equation (5) for polymers

System	n_l	C	$V(P, 0)$	P (bar)	Ref.
PS	0.0637	1.447	0.9378	1.0	17
	0.0758	1.572	0.9313	200.0	17
	0.0772	1.536	0.9219	600.0	17
	0.0687	1.537	0.9177	1000.0	17
	0.0891	1.472	0.9017	1200.0	17
	0.103	1.641	0.9086	1400.0	17
PMMA	0.0521	7.05	0.831	1	20
	0.0468	6.99	0.826	400	20
	0.0439	6.99	0.817	1000	20
	0.0351	6.85	0.811	1600	20
	0.0327	6.82	0.806	2000	20
PSF	0.0971	8.11	0.781	491	21
	0.112	8.44	0.771	981	21
	0.139	9.06	0.761	1471	21

where a subscript y means transition temperature and $y = g$ for T_g, $y = m$ for T_m, and $V_x(P_y, T_y)$ is the volume at P_y, T_y and state x. Values of $F_{y,x}$ for H_2 and Ar at T_m calculated by equation (4) and experimental data published are listed in *Table 2*, where it is shown that T_0 is 4.0 K for the rare-gas solids such as Ar and H_2 and an average value of $F_{m,s}$ is 0.058 for H_2 and 0.0882 for Ar. Evaluation of $V_s(P_y, T_0)$ for solids was made as follows. It is assumed that the V–T relation at constant pressure is expressed by:

$$\ln T = CZ^{n_l} \qquad T \geqslant 1 \tag{5}$$

and

$$Z = [V(P, T) - V(P, 0)]/V(P, T) \tag{6}$$

where C and n_l are constants and are listed in *Table 3*. The usefulness of equation (5) is discussed in ref. 35. Values of $V_s(P_g, 0)$ for polymers are estimated from the P–V–T data available and equation (6). The average values of F_g for PS are $\bar{F}_g = 0.038$, while F_g values for PMMA depend on pressure as shown in *Table 2*.

Typical two-dimensional P–V and P–T cross sections in the P–V–T three-dimensional surface near T_g and T_m observed experimentally are indicated in *Figures 4–6*, where T_g is characterized by the temperature at which the slope in the P–V plot or $(\partial V/\partial P)_T$ in *Figure 4* changes discontinuously and the minimum point in the P–T plot or $(\partial P/\partial T)_V = 0$ in *Figure 5*. On the other hand, in the vicinity of T_m a discontinuous decrease of V with increasing T in the P–V isotherm and a steep rise of P in the P–T isochore shown in *Figure 6* are observed. It is also pointed out that in *Figure 4* the discontinuous points in $(\partial V/\partial P)_T$ are on one P–V isotherm line of T_g at 1 bar. The other point is an inflection point in the

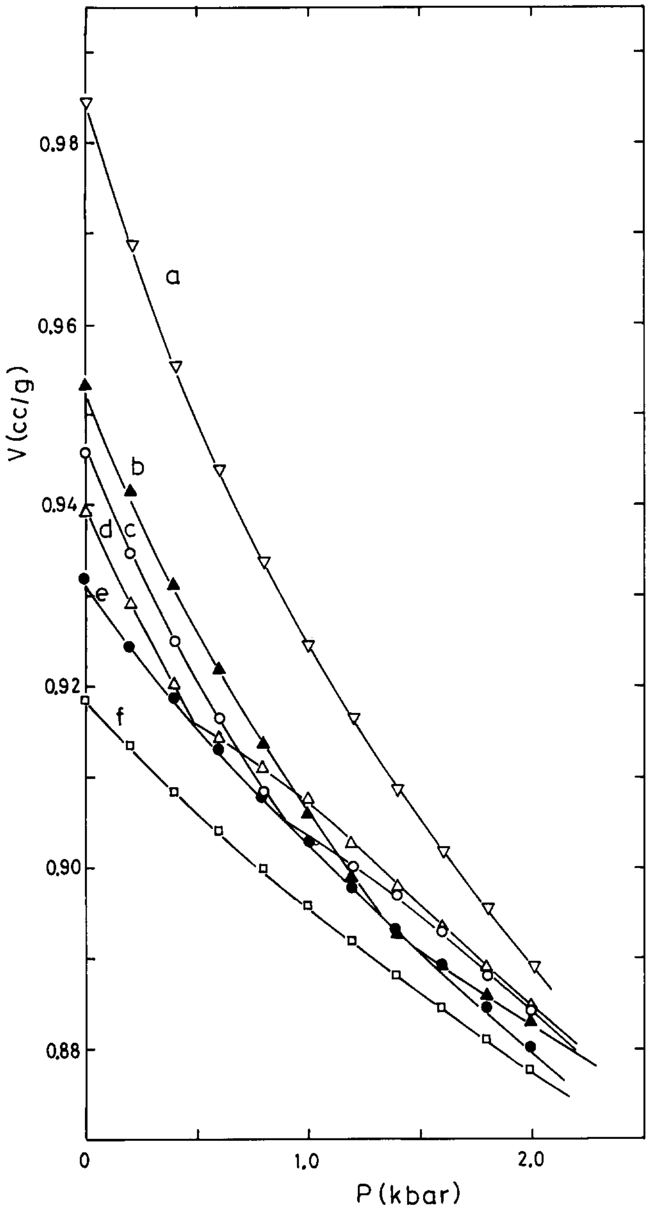

Figure 4 V–P isotherms for poly(cyclohexyl methacrylate) at various temperature: (a) 198.9, (b) 147.3, (c) 134.3, (d) 122.7, (e) 109.6, and (f) 64.0°C. Data are taken from ref. 20

vicinity of T_m in the P–T plot, which is quite similar to that in T_g in *Figure 5*.

The molecular-weight dependence of T_g for polymers is also examined. The quantity F_{g,M_w} is defined as follows:

$$F_{g,M_w}(1, T_g, M_w) = [V(1, T_g, M_w) - V_s(1, 0, M_w)]/V(1, T_g, M_w) \quad (7)$$

where $V(1, T_g, M_w)$ is the volume at 1 bar, T_g and M_w and $V_s(1, 0, M_w)$ is the volume at 1 bar, 0 K and M_w, which can be estimated by using equation (5) and V–T data for various molecular weights at 1 bar[36]. Values of F_{g,M_w} for PS at T_g are listed in *Table 2* where it is shown that an average value of $F_{g,M_w} = 0.053$ obtained from PS with $M_w/M_n = 1.10$ is larger than $F_g = 0.038$ for PS ($M_w/M_n = 3.08$) from the pressure dependence of T_g.

It is very interesting to examine whether the solid–liquid critical point can be found or not on the basis of the experimental data available, although so far the critical point is not observed. It is examined in this work whether $V_{m,s}/V_{m,l}$ becomes 1.0 at a certain pressure where $V_{m,l}$ is the volume of liquid phase and $V_{m,s}$ is the volume of solid phase at T_m. It is assumed that the function of $V_{m,l}$, $V_{m,s}$ and V_g with respect to pressure under T_m or T_g lines is expressed by:

$$V_{y,x}(P=1)/V_{y,x}(P) = A_{y,x}[P + P_{y,x}(T)]^{m_{y,x}} \quad (8)$$

where $V_{y,x}$ means the volume at transition temperature T_y and phase x. Values of $A_{y,x}$, $P_{y,x}$ and $m_{y,x}$ for polymers and rare-gas solids determined from the experimental data are summarized in *Table 4* and $V_{m,s}/V_{m,l}$ calculated by equation (8) against pressure is shown in *Figure 7*, where the possibility of the solid–liquid critical point for polymer is demonstrated. It is obvious that an amorphous polymer does not have T_m. Therefore a semicrystalline polymer with some fraction of amorphous region may have a critical point with increasing pressure if the amorphous region is more compressible than the crystalline region.

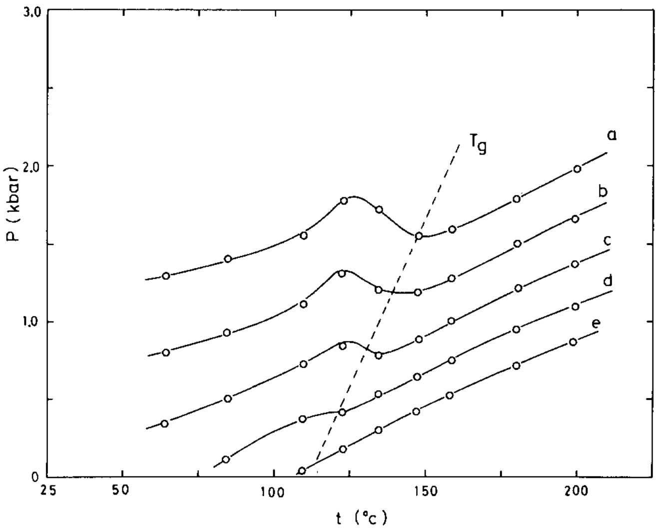

Figure 5 P–t isochore for poly(cyclohexyl methacrylate) at various specific volumes: (a) 0.89, (b) 0.90, (c) 0.91, (d) 0.92, and (e) 0.93 cm^3 g^{-1}; T_g is the P_g–T_g line

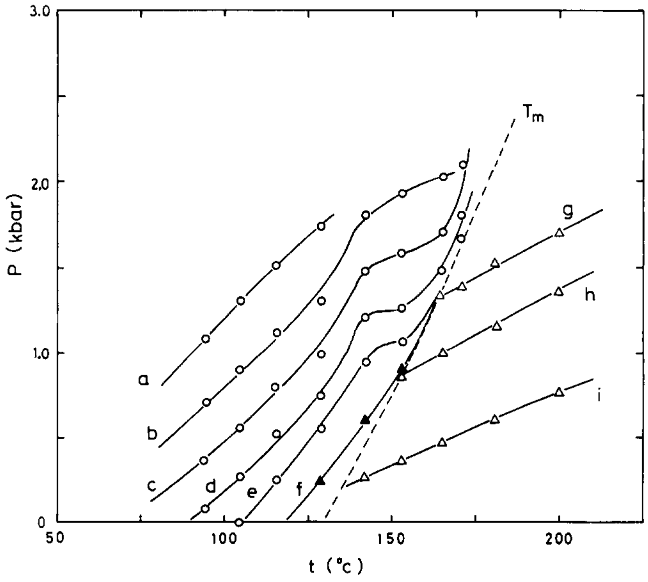

Figure 6 P–t isochore for linear PE at various specific volumes: (a) 1.02, (b) 1.03, (c) 1.04, (d) 1.05, (e) 1.06, (f) 1.08, (g) 1.18, (h) 1.20 and (i) 1.24 cm^3 g^{-1}; T_m is the P_m–T_m line

DISCUSSION

The three-dimensional P–V–T diagram is very useful in discussing the correlation between the equation of state and pressure dependence of T_g and T_m. A schematic P–V–T diagram is shown in *Figure 8* where the experimental behaviour in the vicinity of T_g and T_m shown in *Figures 4–6* is taken into account. It is important to point out that the P–V–T surfaces near T_g and T_m are not smooth and are undulated. The behaviour is observed in PS[17] and polysulphone[21] near T_g and in PE[20], H_2[7] and ^{4}He[11] near T_m. It is also found

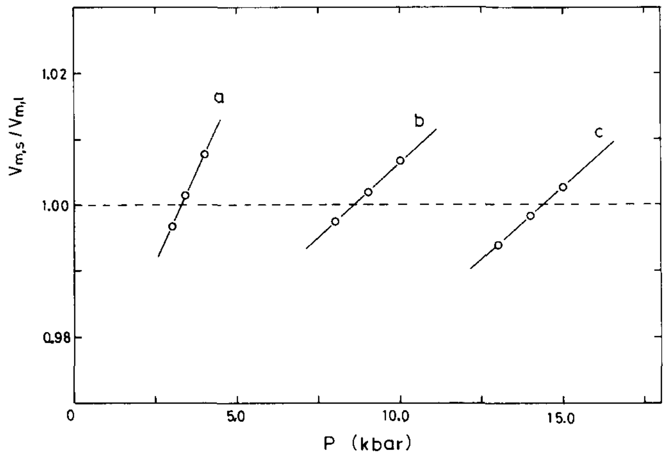

Figure 7 $V_{m,s}/V_{m,l}$ vs. P plot for polyethylene: (a) branched PE, (b) high-molecular-weight PE, and (c) linear PE; $V_{m,s}/V_{m,l} = 1.0$ gives the critical pressure for the solid–liquid line

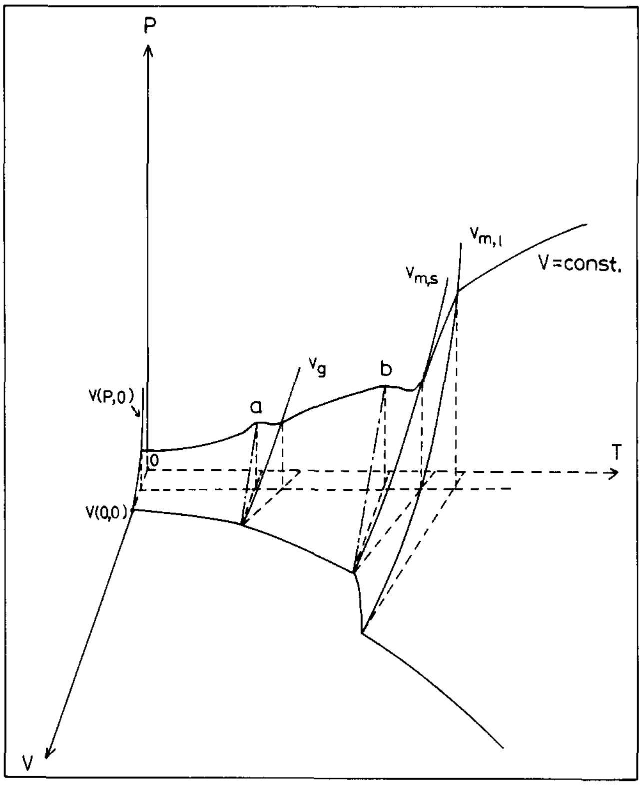

Figure 8 A schematic P–V–T diagram for polymer where V_g is the volume along T_g, $V_{m,s}$ and $V_{m,l}$ are volumes along T_m for solid and liquid phase, respectively. The symbol a is the P–V isotherm at temperature of T_g for 1 bar; b is the P–V isotherm at T_m for 1 bar: $V(P, 0)$ is the P–V isotherm at 0 K

Table 4 Values of $m_{y,x}$, $P_{y,x}$ and $A_{y,x}$ in equation (8)

System	$m_{y,x}$	$P_{y,x}$ (bar)	$A_{y,x}$	$V_{y,x}$ ($P = 1$)	x	P_0 (bar)	Ref.
Ar[a]	0.137	2030	0.3431	0.6835	l	451	3
	0.154	4760	0.2673	0.6093	s	451	3
n-H_2[a]	0.252	1150	0.1123	7.584	l	4733	9
	0.310	4120	0.0599	7.247	s	4733	9
N_2	0.162	2115	0.2892	1.149	l	77.5	16
	0.182	4020	0.2208	1.061	s	77.5	16
Methane	0.152	2480	0.3048	2.207	l	0	16
	0.157	3970	0.2723	2.048	s	0	16
Linear PE	0.0845	1130	0.538	1.228	l	400	20
	0.0171	−310	0.908	1.080	s	600	20
Branched PE	0.1775	4300	0.228	1.240	l	1	20
	0.1055	5300	0.400	1.161	s	600	20
High-M_w PE	0.0698	1060	0.608	1.251	l	200	20
	0.0205	−131	0.876	1.144	s	800	20
PP	0.1037	932	0.492	1.302	l	1	28
	0.2285	5640	0.139	1.182	s	1	28
PET	0.0606	1991	0.2245	0.761	l	1	22
	0.0387	251	0.8075	0.851	s	1	22
Poly(but-1-ene)	0.0866	868	0.557	1.246	l	1	28
	0.109	1795	0.441	1.158	s	1	28
PS	0.0966	2740	0.4637	0.9673	g	1	17
PMMA[a]	0.0994	2880	0.4532	0.8620	g	1	20
PSF	0.0760	5100	0.5228	0.8376	g	1	21

[a] The P–V isotherms for Ar and n-H_2 are $0.5647/V = 0.2596(P + 4800)^{0.159}$ at 4.0 K for Ar and $11.24/V = 0.233(P + 579)^{0.233}$ at 4 K for n-H_2, while that for PMMA is $0.8620/V = 0.4531(P + 2880)^{0.0994}$ at 374.1 K[20]

experimentally that the V_g–P_g line is nearly equal to the V–P isotherm at temperature T_g at 1 bar in PS[17] and poly(cyclohexyl methacrylate)[20] and the V_m–P_m line for T_m is nearly equal to the V–P isotherm at temperature 4K in n-H_2 and Ar (see *Table 4*). These results suggest the existence of a flat strip region in the P–V–T surface in the vicinity of T_g and T_m as is shown in *Figure 8*.

The Gibbs free energy can be determined using equation (2) for a solid and liquid by:

$$G = \int V\,\mathrm{d}P = [V_x(1, T)/(1 - m_x)A_x] \times [P + P_x(T)]^{1-m_x} + g(T) \qquad (9)$$

where $g(T)$ is a function of temperature. It is speculated from this work that the Gibbs free energy function, equation (9), does not change over the temperature region including T_g because m_x is almost constant over T_g although P_x changes discontinuously with increasing temperature at T_g. On the other hand, the Gibbs free energy function does change at T_m, at which m_l changes discontinuously. The result shows the validity of the Ehrenfest equation on the phase transition. It is also suggested that the P–V–T surface over T_g is originally a smooth surface and suddenly a part of the P–V–T surface slipped down along the T_g line at T_g. Therefore the Gibbs free energy function below T_g is the same as that above T_g and a distortion in the P–V–T surface near T_g is taken as the trace of slipping.

It is very interesting to refer to theoretical and experimental work on the transition temperature and its pressure dependence. Lindemann[37] postulates that melting occurs when the amplitude of atomic vibration has become about 10% of the distance of separation of atomic centres at 0K. The invariance of the liquid order along the freezing curve has been discussed through the pair distribution function at different temperatures using the Monte Carlo method[5]. The results can be compared with values of $F_m = 5.8\%$ for H_2 and 8.82% for Ar, which are independent of pressure approximately. It is speculated from this work, that a solid–liquid critical point may exist in a semicrystalline polymer such as branched PE at 200°C, 3300 bar, in high-molecular-weight PE at 380°C, 8700 bar and in linear PE at 400°C, 14400 bar, where the critical temperatures are estimated from a linear relation between T_m and P_m and the critical pressure is estimated from *Figure 7*.

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