Semi-empirical equation on temperature dependence of heat capacity for polymers and simple liquids

S. Saeki, M. Tsubokawa and T. Yamaguchi
Department of Polymer Engineering, Fukui University, Fukui 910, Japan

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The semi-empirical equation for heat capacity at constant volume C_v is proposed from the standpoint of the homogeneous function approach and applied to polymers (polystyrene and poly(methyl methacrylate) over the temperature range 0.1–4.0 K, polyethylene over 1–400 K and poly(tetrafluoroethylene) over 1–360 K) and simple liquids (argon, methane, n-heptane, carbon tetrachloride and benzene) from the triple point to the gas–liquid critical point T_c, using data published by many authors. The equation derived in this work is

$$C_v = c_1(Y^{d_0}/T)\exp(-c_0^{-1}I_{d_0})$$

where I_{d_0} is defined by $I_{d_0} = \int_{Y_0}^{Y} Y^{d_0}/(1+Y)\,dY$, $Y = (T_c - T)/T$ and $c_1, c_0, Y_0 \approx 0$ and d_0 are constants. For simple liquids, C_v is expressed by

$$C_v = c_1(Y^{d_0}/T)\exp\{-c_0^{-1}Y^{d_0+1}/(d_0+1)\}$$

under the condition $Y \ll 1.0$, and the value of d_0 estimated from the experimental data is -0.10, which suggests that $C_v \propto (T_c - T)^{-0.10}$ near T_c. The equation for C_v for polymers is expressed by

$$C_v = c_1^* T^{a_0}$$

and the value of a_0 obtained in this work is ≈ 3.0 over 1–4 K, while $a_0 \approx 1.0$ over 30–400 K and 0.1–0.4 K. It is found in this work that the heat capacity function $C_v = AT + BT^3$ observed in amorphous polymers below 4 K can be predicted by the semi-empirical equation for C_v. Deviations of C_v from the Debye model in the extremely low temperature region are discussed, based on the experimental and theoretical work of many authors.

(Keywords: heat capacity; Debye T^3 law; critical exponent; simple liquid; semi-empirical C_v equation)

NTRODUCTION

ecently, much attention has been paid to the emperature dependence of heat capacity, both heoretically and experimentally, in relation, first to the eviation of C_v of amorphous polymers below 1 K from he Debye model[1-3] characterized by $C_v \sim T^3$ and, econdly, to the critical exponent of C_v for simple liquids t the critical point expressed by α and $C_v \propto (T_c - T)^{-\alpha}$ Reference 4).

It is well known that most solids obey the $C_v \sim T^3$ law ver the low temperature range. Wunderlich[5] predicted he temperature dependence of C_v for completely rystalline polyethylene (PE) based on the Tarasov odel[6], where a three-dimensional Debye term for the west frequencies and a one-dimensional Debye term for he higher frequencies are used, and obtained good greement between the theoretical and experimental alues over 1–150 K. For temperatures > 150 K, low-equency optical vibrations contribute to the specific eat in PE[5]. However, recent work on the heat capacity $_v$ of non-crystalline polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) and non-crystalline dielectric solids below 1 K shows a deviation from the Debye model, which is summarized as: $C_v = AT + BT^3$, where A and B are constants[1-3]; a higher heat capacity than that of the Debye model[7-10]; and abnormal excess heat capacity with a maximum[1] or a plateau[8].

It is known that the exponent α of C_v is 0.10 [4]. However, to our knowledge, there are no reports on the relation between the temperature dependence of C_v near the critical point and that over the temperature range far from T_c. In this work we have tried to find a semi-empirical equation for C_v on the basis of the thermodynamic equation and the homogeneous function method which can apply to liquids and solids, including crystalline and non-crystalline or amorphous solids.

DERIVATION OF SEMI-EMPIRICAL EQUATION FOR C_v

In this calculation we have used two assumptions: first, the internal energy $E(T,V)$ is separated into two terms

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$E(T,V)=E(T)+E(V)$; and, secondly, $E(T)$ is expressed by a homogeneous function of $T/(T_c-T)$. The expression for $E(T,V)$ is then given by

$$E(T,V)=c_0C_vT\{T/(T_c-T)\}^{d_0}+E(V) \qquad (1)$$

where c_0 and d_0 are constants but depend on the state of the system, or the temperature range for solids. From equation (1) and the thermodynamic equation $C_v=(\partial E/\partial T)_v$ it can be derived that

$$c_0^{-1}\{T/(T_c-T)\}^{-d_0}/T=(\partial C_v/\partial T)_v/C_v+T^{-1} +d_0\{T^{-1}+(T_c-T)^{-1}\} \qquad (2)$$

where the conditions $T\neq 0$ and $T\neq T_c$ are used. Integration of equation (2) with respect to temperature at constant volume has been carried out from T to T_0, where T_0 is a temperature close to T_c. The resulting equation is

$$\ln C_v(T)=d_0\ln\{(T_c-T)/T\}-c_0^{-1}\int_T^{T_0}\{(T_c-T)/T\}^{d_0}/T\,\mathrm{d}T -\ln T+\ln c_1 \qquad (3)$$

where c_1 is an integration constant and a function of volume in general. In this case c_1 is taken as a constant because $E(T,V)=E(T)+E(V)$ and is expressed using equation (3) by

$$\ln c_1=\ln C_v(T_0)+\ln T_0-d_0\ln\{(T_c-T_0)/T_0\} \qquad (4)$$

The expression of C_v as a function of temperature is given using equation (3) by

$$C_v(T)=c_1[\{(T_c-T)/T\}^{d_0}/T]\exp(-c_0^{-1}I_{d_0}) \qquad (5)$$

where I_{d_0} is defined by

$$I_{d_0}=\int_T^{T_0}\{(T_c-T)/T\}^{d_0}/T\,\mathrm{d}T \qquad (6)$$

The internal energy $E(T,V)$ is obtained by

$$E(T,V)=c_0c_1\exp(-c_0^{-1}I_{d_0})+E(V) \qquad (7)$$

It is noteworthy that C_v in equation (5) becomes infinite at the limit $T=T_c$ and approaches zero at the limit $T=0$ if $d_0<-1.0$.

DETERMINATION OF HEAT CAPACITY C_v AS A FUNCTION OF TEMPERATURE NEAR T_c AND $T=0$ K

The heat capacity C_v of simple liquids near T_c is derived using a variable Y defined by

$$Y=(T_c-T)/T \qquad (8)$$

The integration of equation (6) is transformed, using Y, to

$$I_{d_0}=-\int_Y^{Y_0}Y^{d_0}/(1+Y)\,\mathrm{d}Y \qquad (9)$$

where $Y_0=(T_c-T_0)/T_0\approx 0$. Near T_c, $Y_0<Y\ll 1$, I_{d_0} is given by

$$I_{d_0}=Y^{d_0+1}/(d_0+1) \qquad (10)$$

It is derived from equations (5) and (10) that

$$\ln C_vT=\ln c_1+d_0\ln Y-Y^{d_0+1}/\{c_0(d_0+1)\} \qquad (11)$$

On the other hand, near $T=0$ K C_v is derived, using equation (5), as

$$C_vT=c_1(T_c/T)^{d_0}\exp[-c_0^{-1}\{K-\delta_0\ln(T_c/T)\}] \qquad (12)$$

where K and δ_0 are constants and the approximations $T_c\gg T$ or $Y=T/T_c$ and $I_{d_0}=K-\delta_0\ln(T_c/T)$ are used. In the latter approximation we intended to express C_v as a function of T alone and C_v is given using equation (12) by

$$C_v=c_1^{*}T^{(-d_0-c_0^{-1}\delta_0-1)} \qquad (13)$$

where $c_1^{*}=c_1\exp(-c_0^{-1}K)/T_c^{(-d_0-c_0^{-1}\delta_0)}$ is a constant.

RESULTS

Experimental data for C_v as a function of temperature are available for the simple liquids[4] argon, methane, n-heptane, carbon tetrachloride and benzene, and polymers PS[2,7], PMMA[2,7], PE[5,11] and poly(tetrafluoroethylene) (PTFE)[10,12,13].

The evaluation of d_0 in simple liquids was done by a trial and error method until a linear relation between $\ln(C_vT)-d_0\ln Y$ and Y^{d_0+1} was obtained. Typical plots are given in *Figures 1–3*, where linearity is observed over a wide temperature range with $d_0=-0.10$. The linearity is also observed in benzene and carbon tetrachloride with $d_0=-0.10$. It is proposed that the heat capacity of liquids is expressed by

$$C_vT=c_1Y^{-0.10}\{\exp(c_2Y^{0.90})\} \qquad (14)$$

where $c_2=-1/0.9c_0$ is a constant.

Values of $(-d_0-c_0^{-1}\delta_0-1)$ in equation (13) are determined for PS, PMMA, PE and PTFE using the

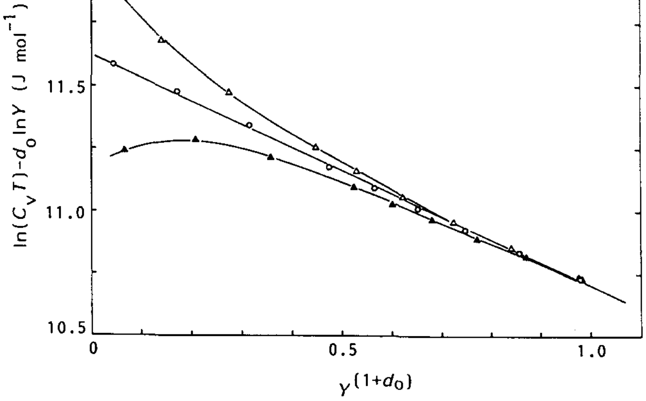

Figure 1 $\ln(C_vT)-d_0\ln Y$ *versus* $Y^{(1+d_0)}$ for n-heptane with, △, $d_0=0$; ○, $d_0=-0.10$; and, ▲, $d_0=-0.20$; $Y=(T_c-T)/T$. Data are taken from Reference 4

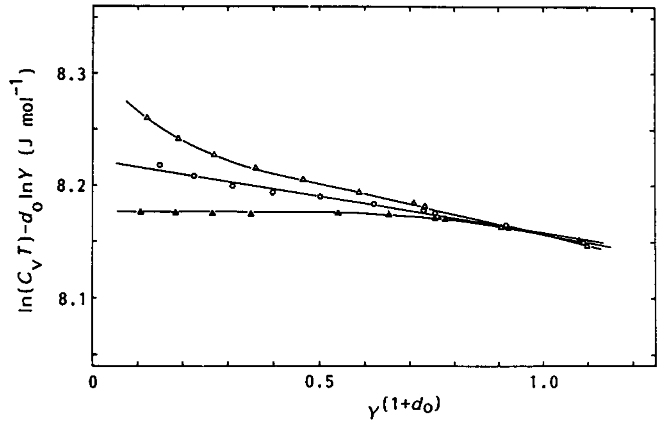

Figure 2 $\ln(C_vT)-d_0\ln Y$ *versus* $Y^{(1+d_0)}$ for methane with, △, $d_0=0$; ○, $d_0=-0.10$; and, ▲, $d_0=-0.20$. Data are taken from Reference 4

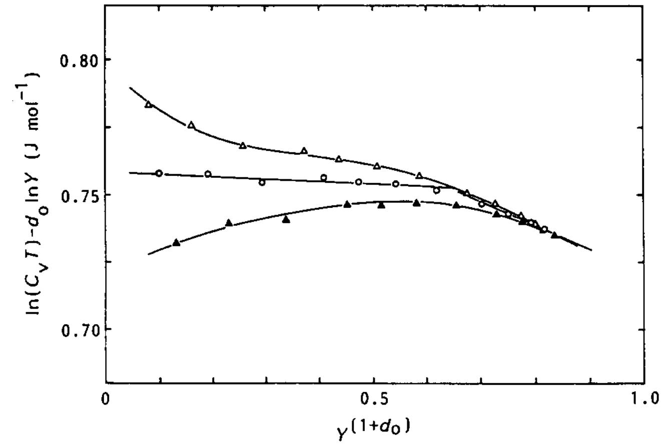

Figure 3 $\ln(C_vT)-d_0\ln Y$ *versus* $Y^{(1+d_0)}$ for argon with, △, $d_0=0$; ○, $d_0=-0.10$; and, ▲, $d_0=-0.20$. Data are taken from Reference 4

relation

$$\ln C_v = \ln c_1^* + a_0 \ln T \qquad (15)$$

where $a_0=-d_0-c_0^{-1}\delta_0-1$. The plot is shown in *Figure 4*, where linearities are observed in the three temperature regions $\ln T < -1.0$, $0 < \ln T < 1.4$ and $\ln T > 3.4$. It is obtained from the slope in *Figure 4* that over the temperature range 1–4 K C_v is proportional to T^3, while for $T > 30$ K and $0.1 < T < 0.36$ K C_v is proportional to T. The solid lines in *Figure 4* indicate the T and T^3 dependences of C_v. A deviation from the Debye T^3 law occurs at a temperature <0.36 K in the amorphous polymers such as PS and PMMA. The temperature dependence of C_v is approximated over the low temperature region 0.1–4 K by

$$C_v = AT + BT^3 \qquad (16)$$

where A and B are constants.

DISCUSSION

It is interesting to examine the temperature dependence of C_v based on the experimental data[4]. In n-heptane C_v has a linear temperature dependence in the liquid state except near the gas–liquid critical point, while C_v is almost constant in methane and argon, for example $C_v/R=3.7$–4.0 for methane and 2.2–2.4 for argon[4]. A typical temperature dependence of C_v for the liquids is analysed using equation (11) in *Figure 5*, where $\ln(C_vT)$ for n-heptane is separated into two terms: one approaches zero and the other diverges infinitely on approaching T_c. It is shown in *Figure 5* that the latter term gives a finite

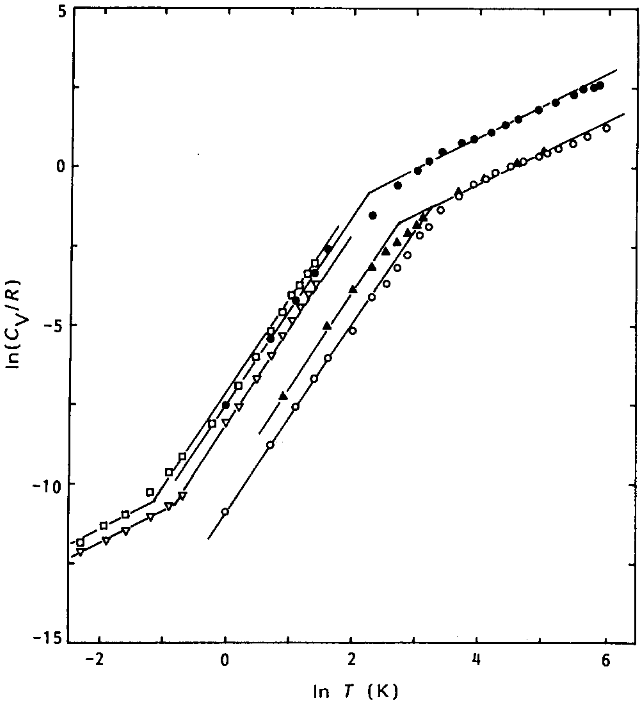

Figure 4 $\ln(C_v/R)$ *versus* $\ln T$ for polymers: □, PS[2,7]; ▽, PMMA[2,7]; ○, crystalline PE[5]; ▲, amorphous PE[11]; ●, PTFE[10,12,13]

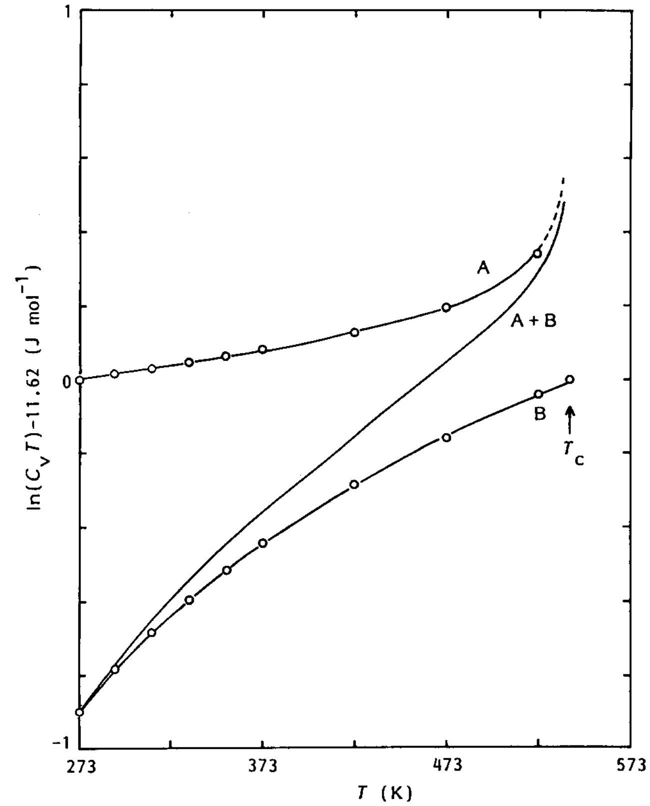

Figure 5 The two terms in $\ln(C_vT)$ for n-heptane *versus* temperature T, from equation (11), $\ln C_vT=\ln c_1+d_0\ln Y-Y^{d_0+1}/\{c_0(d_0+1)\}$. Curve A is for $d_0\ln Y=-0.10\ln Y$; curve B is for $-Y^{d_0+1}/\{c_0(d_0+1)\}=-0.9125Y^{0.9}$; and curve A+B is the sum of A and B. The value of 0.9125 is determined from the slope in *Figure 1*. The total $\ln(C_vT)$ is expressed by $\ln(C_vT)=11.62-0.10\ln Y-0.9125Y^{0.9}$, where $\ln c_1=11.62$ (J mol^{-1}) is determined using data from *Figure 1*

contribution to C_v over the temperature region far from T_c.

It is important to discuss the deviation of the heat capacity of non-crystalline solids from the Debye law $C_v \sim T^3$ in the low temperature region below 1 K. It is confirmed experimentally by many authors that the linear temperature dependence of C_v below 1 K is a general and important phenomenon characterizing the heat capacity of non-crystalline solids[1-3]. Even at temperatures <4 K where T^3 behaviour is found, the heat capacity data departs significantly from the Debye theory[7-10]. Many attempts to explain the origin of the linear temperature dependence of C_v and excess heat capacity from the Debye theory have been made[1-3,7-10,14]. For example, a theoretical explanation of the linear dependence of C_v was proposed by Phillips using an ionic tunnelling model[14], while Zeller and Pohl tried to attribute it to motional states of ions, trapped atoms or large groups of atoms, or one-dimensional vibrations within a three-dimensional solid[2]. The magnitude of the heat capacity for amorphous polymers determined experimentally is about 100% or more higher than that calculated from the sound velocity measurement using the Debye equation. Rosenstock[15] has suggested the presence of cavities in the disordered structure, while Choy *et al.*[9] indicate that localized vibrational modes in the amorphous phase are responsible for the excess heat capacity.

It is interesting to explain the linear temperature dependence of C_v using the equations in this work. The expression for the heat capacity near $T = 0$ K is derived using equation (3) by replacing T_0 with $T_0^* \approx 0$ K and equation (5) with approximations

$$T/(T_c - T) \sim T/T_c$$

and

$$I_0 = \int_T^{T_0^*} (T_c/T)^{d_0}/T \, \mathrm{d}T$$

$$= -(T_c^{|d_0|}|d_0|)^{-1}(T^{|d_0|} - T_0^{*|d_0|}) \quad (17)$$

using $d_0 = -|d_0|$. The expression is

$$C_v T = c_1'(T/T_c)^{|d_0|}\exp\{-T_0^{*|d_0|}/(c_0|d_0|T_c^{|d_0|})\}\exp\{(T^{|d_0|}/(c_0|d_0 T_c^{|d_0|})\}$$

$$= c_1'(T/T_c)^{|d_0|}\exp\{-T_0{}^{*|d_0|}/(c_0|d_0|T_c^{|d_0|})\}[1 + T^{|d_0|}/(|d_0|T_c^{|d_0|}c_0)$$

$$+ \{(|d_0|!)^2/(2|d_0|!)\}T^{2|d_0|}/(|d_0|T_c^{|d_0|}c_0)^2 + \ldots] \quad (18)$$

where $c_1' = C_v(T_0^*)T_0^*\{T_0^*/(T_c - T_0^*)\}^{d_0}$ is a constant. Equation (18) is simplified as

$$C_v = K_1 T^{(|d_0| - 1)} + K_2 T^{(2|d_0| - 1)} + \ldots \quad (19)$$

where K_1 and K_2 are constants. If it is assumed that $d_0 = -2.0$, then near $T = 0$ K C_v is given by

$$C_v = K_1 T + K_2 T^3 + \ldots \quad (20)$$

which is a function of temperature similar to equation (16). For $d_0 = -1.0$, C_v is expressed by

$$C_v = K_1' + K_2' T + K_3' T^2 + \ldots \quad (21)$$

which does not satisfy the condition that $C_v \rightarrow 0$ in the limit $T \rightarrow 0$ K. It is suggested that equation (5) with $d_0 = -2.0$ or equation (20) gives a characteristic feature of C_v in the low temperature range for non-crystalline solids. The ratio K_2/K_1 in equation (20) is calculated using equation (18):

$$K_2/K_1 = (2c_0 T_c^2)^{-1} \quad (22)$$

where K_1 is approximated by c_1'/T_c^2 due to $\exp(-T_0^*/c_0|d_0|T_c^{|d_0|}) \sim 1.0$. Values of K_1 and K_2 are determined experimentally[2], for example $K_1 = 52 \times 10^{-7}$ J g^{-1} K^{-2} and $K_2 = 460 \times 10^{-7}$ J g^{-1} K^{-4} for PS[2]. It is obvious from the values of K_1 and K_2 that the contribution of the $K_1 T$ term to C_v becomes significant over the temperature range around 0.1 K, while the T^3 term becomes more dominant at a temperature >1 K, which is demonstrated in *Figure 6*, where $\ln C_v \sim \ln\{T + (K_2/K_1)T^3\}$ is plotted against $\ln T$ for various ratios K_2/K_1.

It is very interesting to refer to the theoretical prediction of C_v for crystalline polymers. The most useful theory of C_v for crystalline polymers is that proposed by Tarasov, which leads to the T^3 dependence of C_v at low temperature, while the T^2 dependence of C_v is discussed by Tarasov[16], Gurney[17] and Stockmayer[18]. Wunderlich[5] also proposed a more detailed model based on the Tarasov model where vibrations in the crystalline polymer are taken into account. Lee and Choy showed that the heat capacity of fluoropolymers is reasonably explained by the Tarasov model[19]. On the other hand Swaminanthan and Tewari[20] proposed an anisotropic dispersive continuum model and successfully explained the experimental results for the heat capacity of PE of any degree of crystallinity.

In this work we have focused on a characteristic feature of the temperature dependence of the heat capacity for liquids and solids and tried to explain the behaviour using a semi-empirical equation and the experimental data. It

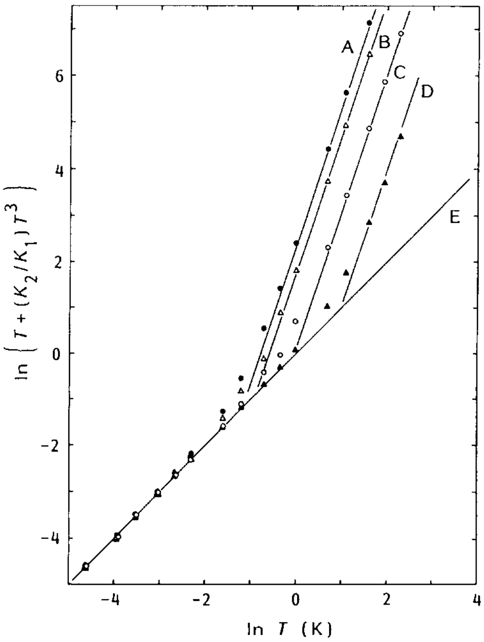

Figure 6 $\ln\{T + (K_2/K_1)T^3\}$ *versus* $\ln T$ for various values of K_2/K_1: A, 10; B, 5; C, 1.0; D, 0.1; E, 0. The slope of line E is 1.0, corresponding to $C_v \sim T$, while the steeper slope in lines A–D is 3.0, corresponding to $C_v \sim T^3$

was speculated that an index d_0 in equation (5) plays an important role in predicting the temperature dependence of C_v and depends on the state of the system sensitivity. In a liquid state $d_0 = -0.10$ explains the heat capacity over the entire range of liquid state, including the critical region. On the other hand, in a non-crystalline solid $d_0 = -2.0$ can predict $C_v = AT + BT^3$ over the low temperature range, including the extremely low temperature range < 1 K, while in a crystalline solid d_0 may be equal to -4.0 if C_v is expressed by $C_v = BT^3$ over the low temperature range, including < 1 K. Although we cannot yet explain the physical meaning of d_0, useful information on heat capacity over a wide range of temperatures has been found. It is seen from *Figure 4* that the heat capacity of non-crystalline solids such as amorphous polymers indicates a discontinuous change from $C_v \sim T$ to $C_v \sim T$ through the $C_v \sim T^3$ region with increasing temperature, which is similar to the behaviour in the neighbourhood of the glass transition temperature for polymers with respect to the discontinuity of the heat capacity.

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