

Calculation of Temperature and Pressure Dependence of Heat Capacities in Polymer Melts

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Synopsis

A new PVT equation of state $\overline{P}\overline{V}^s = \overline{T}^y - \ln \overline{V}$ where $\overline{P} = P/B_0$, $\overline{V} = V/V_0$, and $\overline{T} = T/T_0$, was used to calculate the temperature and pressure dependence of $C_p - C_v$ for polymer melts. The results are in the form of universal master curves in terms of reduced variables. As a function of temperature, a maximum in $C_p - C_v$ is predicted, while as a function of pressure a minimum is predicted. Supplementing the PVT equation with experimental $C_p(T)$ data from the literature, C_p/C_v was also found to have a maximum as a function of temperature. Two useful approximations were also found. One is related to the Nernst-Lindemann equation for $C_p - C_v$ and the other is the approximate constancy of RT_0/B_0V_0 .

INTRODUCTION

Heat capacity is a fundamental thermodynamic polymer property. Although measurements are almost always made of the heat capacity at constant pressure C_p , theories are often more conveniently expressed in terms of the heat capacity at constant volume C_v . The difference between the two values can be calculated from the thermodynamic relation

$$C_p - C_v = T V \alpha^2 B_T M \quad (1)$$

where T is absolute temperature, V is specific volume, α is the thermal expansion coefficient, B_T is the isothermal bulk modulus, and M is molecular weight (so that the molar heat capacities are obtained). This equation is difficult to use because the input data is generally not available, especially as a function of temperature and pressure.

Recently, a pressure-volume-temperature (PVT) equation of state for polymer melts was derived and shown to fit the measured volume data for polymer melts very accurately.¹ (We will use the term polymer melt to include both crystalline polymers above the melting point and amorphous polymers above the glass transition.) An advantage of this equation is its simple analytic form which allows calculations of derivatives, such as α and B_T , as functions of temperature and pressure. The PVT equation of state can also be used to calculate the pressure dependence of C_p , another fundamental property difficult to measure.

In some applications, it is not the difference of the heat capacities, $C_p - C_v$, that is required but their ratio, C_p/C_v . For example, to convert an acoustically measured bulk modulus, which is an adiabatic value B_S to the isothermal value B_T , the thermodynamic relation

$$B_S/B_T = C_p/C_v \quad (2)$$

is used. This ratio cannot be calculated solely in terms of PVT properties. A value of $C_p(T)$ must be determined independently.

In this paper, we will use the previously derived PVT polymer melt equation of state to calculate $C_p - C_v$ as a function of temperature and pressure and C_p as a function of pressure. Taking experimental $C_p(T)$ values, at zero pressure, from the literature, calculations will be made of C_p/C_v as a function of temperature. When PVT data are not available, approximations are useful. We will examine the Nernst-Lindemann relation and also a new approximation based on the equation of state. Whenever possible, comparisons with experimental data will be made.

HEAT CAPACITY DIFFERENCE

To calculate $C_p - C_v$ from eq. (1), the equation of state used is given by

$$\bar{P}\bar{V}^5 = \bar{T}^{3/2} - \ln \bar{V} \quad (3)$$

where the reduced variables are $\bar{P} = P/B_0$, $\bar{T} = T/T_0$, and $\bar{V} = V/V_0$ and B_0 , T_0 , and V_0 are characteristic parameters for each polymer. From eq. (3) it follows that

$$\alpha = (3T^{1/2}/2T_0^{3/2}) [1 + 5\bar{P}\bar{V}^5]^{-1} \quad (4)$$

$$B_T = B_0/\bar{V}^5 + 5P \quad (5)$$

It then follows from eq. (1) that

$$(C_p - C_v)/R = (9M/4)(B_0V_0/RT_0)(\bar{T}^2/\bar{V}^4)(1 + 5\bar{P}\bar{V}^5)^{-1} \quad (6)$$

Defining a dimensionless reduced heat capacity difference as

$$\bar{C}_p - \bar{C}_v = (4RT_0/9MB_0V_0)(C_p - C_v) \quad (7)$$

Equation (6) can be expressed in terms of reduced variables only:

$$\bar{C}_p - \bar{C}_v = (\bar{T}^2/\bar{V}^4)(1 + 5\bar{P}\bar{V}^5)^{-1} \quad (8)$$

A plot of $\bar{C}_p - \bar{C}_v$ vs. \bar{T} is given in Figure 1. As shown there, $\bar{C}_p - \bar{C}_v$ goes through a maximum at a certain reduced temperature. This is the first time, to our knowledge, that such a prediction has been made. Let us look at the origin of this behavior more closely. For convenience, consider first the behavior at zero pressure, where most measurements will be made. At $P = 0$, eq. (3) becomes

$$\ln \bar{V} = \bar{T}^{3/2} \quad (P = 0) \quad (9)$$

and therefore

$$\bar{C}_p - \bar{C}_v = \bar{T}^2 \exp(-4\bar{T}^{3/2}) \quad (10)$$

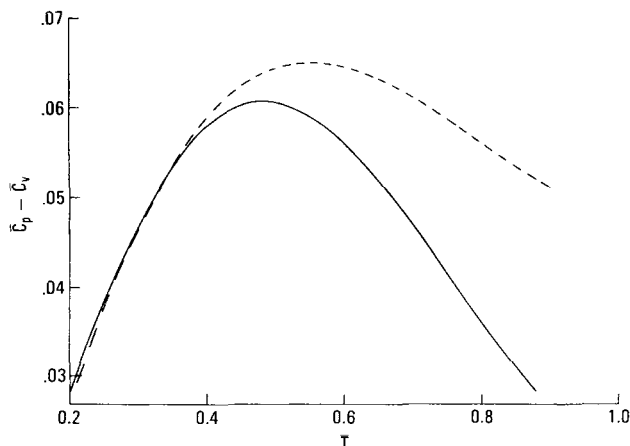


Fig. 1. Reduced heat capacity difference vs. reduced temperature: (—) $\bar{P} = 0$; (---) $\bar{P} = 0.067$.

Thus, $\bar{C}_p - \bar{C}_v$ at first increases with temperature as a result of the \bar{T}^2 factor and then decreases as a result of the $\exp(-4\bar{T}^{3/2})$ factor. The physical basis for the maximum is that at high enough temperature, the increase of $TV\alpha^2$ with temperature is dominated by the decrease of B_T with temperature.

The peak in $\bar{C}_p - \bar{C}_v$ occurs at a reduced temperature of $\bar{T} = 3^{-2/3} = 0.481$. For many polymers, this corresponds to a temperature higher than the degradation temperature. For linear polyethylene, for example, by fitting to the PVT data of Olabisi and Simha,² it was found¹ that $T_0 = 1203$ K. The maximum in $C_p - C_v$ is then predicted to occur at 579 K for $P = 0$, a temperature beyond the range where the PVT measurements were made. A plot of $C_p - C_v$ vs. temperature for polyethylene is given in Figure 2. Over the range of temperature used in the PVT measurements, $C_p - C_v$ is an increasing function of temperature and the effect of pressure, up to 2 kbar, is relatively small. (To make the calculations at 2 kbar, the other two reducing parameters must be known: $V_0 = 1.0362$ cm³/g, $B_0 = 28.0$ kbar).

The opposite temperature dependence is predicted for polytetrafluoroethylene. In this case, the PVT data of Zoller³ yields $T_0 = 875$ K so that

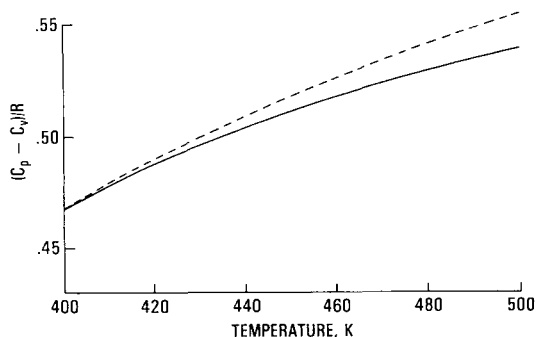


Fig. 2. Heat capacity difference vs. temperature for polyethylene: (—) $P = 0$; (---) $P = 2$ kbar.

the maximum occurs at 421 K. Since the melting point, at zero pressure, of polytetrafluoroethylene is 600 K, all of the measurements in the melt will be above the maximum, i.e., in the region where $C_p - C_v$ decreases with increasing temperature, as shown in Figure 3. In this case, the temperature behavior is opposite to that of polyethylene and the pressure dependence is larger. (The other reducing parameters are $V_0 = 0.3592 \text{ cm}^3/\text{g}$ and $B_0 = 36.4 \text{ kbar}$.) One other polymer where one might see decreasing $C_p - C_v$ vs. temperature is polydimethylsiloxane. Using the data of Shih and Flory,⁴ it was found¹ that $T_0 = 999 \text{ K}$, $V_0 = 0.8782 \text{ cm}^3/\text{g}$, and $B_0 = 18.5 \text{ kbar}$. For temperatures above 480 K then, $C_p - C_v$ should decrease with temperature.

The pressure dependence of $\bar{C}_p - \bar{C}_v$ can also be determined from eq. (8) with the results shown in Figure 4. In this case, there is a minimum value as a function of pressure. Note, however, that the minimum is only about 2% lower than the $\bar{P} = 0$ value. Thus, a fairly accurate experimental procedure would be required to measure this effect. As an example, in terms of unreduced variables, for polystyrene $(C_p - C_v)/R$ as a function of pressure is given in Figure 5. PVT data was taken from Quach and Simha,⁵ and it was found¹ that $T_0 = 1581 \text{ K}$, $V_0 = 0.8732 \text{ cm}^3/\text{g}$, and $B_0 = 29.7 \text{ kbar}$.

HEAT CAPACITY

In this section, we will first consider the pressure dependence of C_p . (The behavior of C_v then follows from the results of the previous section.) From basic thermodynamics,

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P = -TV\alpha^2 \left[1 + \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T}\right)_P\right] \quad (11)$$

Using either equation, the pressure derivative can be calculated from the

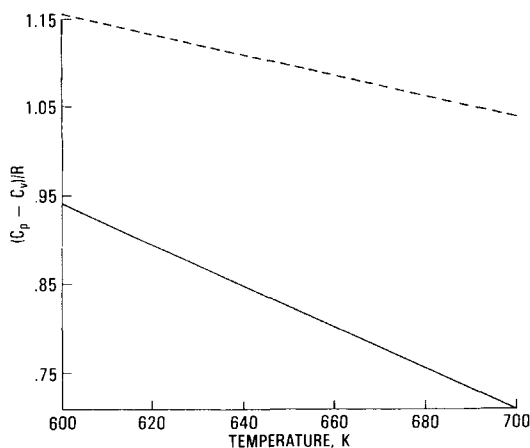


Fig. 3. Heat capacity difference vs. temperature for polytetrafluoroethylene: (—) $P = 0$; (---) $P = 2 \text{ kbar}$.

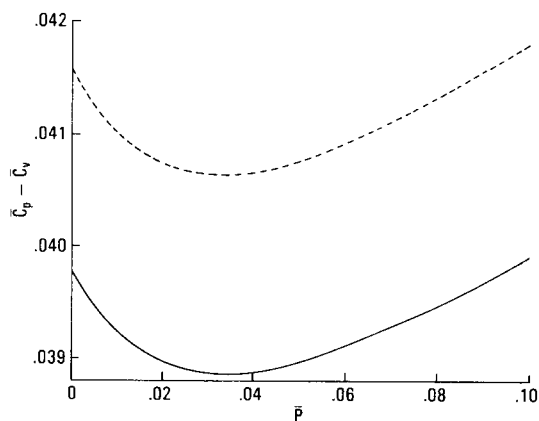


Fig. 4. Reduced heat capacity difference vs. reduced pressure: (—) $\bar{T} = 0.26$; (---) $\bar{T} = 0.27$.

PVT equation of state, with the result that

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -\frac{3}{2} \frac{V_0}{T_0} \left[\frac{\bar{T}^{1/2} \bar{V}}{2X} + \frac{3\bar{T}^2 \bar{V}}{2X^2} - \frac{75\bar{T}^2 \bar{P} \bar{V}^6}{2X^3} \right] \quad (12)$$

$$X = 1 + 5\bar{P}\bar{V}^5 \quad (13)$$

This equation can be integrated to yield

$$\begin{aligned} C_p(T, P) - C_p(T, 0) = & -\frac{3}{2} \frac{B_0 V_0}{T_0} \left[\frac{\bar{T}^{1/2}}{8} [\bar{V}^4(P) - \bar{V}^4(0)] \right. \\ & - \frac{3}{2} \bar{T}^2 (\bar{V}^{-4}(P) \{5[\bar{T}^{3/2} - \ln \bar{V}(P)] + 1\}^{-1} \\ & \left. - \bar{V}^{-4}(0) \{5[\bar{T}^{3/2} - \ln \bar{V}(0)] + 1\}^{-1}) \right] \quad (14) \end{aligned}$$

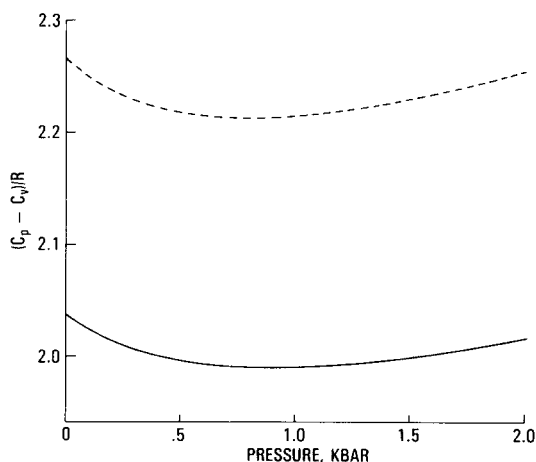


Fig. 5. Heat capacity difference vs. pressure for polystyrene: (—) $T = 450$ K; (---) $T = 500$ K.

According to Eq. (14), C_p should decrease as the pressure increases. Such behavior has been observed experimentally for solid polymers.⁶ For poly(methylmethacrylate), polystyrene, and isotactic polypropylene, a decrease of about 5% was measured at the highest pressure used, 37 kbar. Karl⁷ et al. attempted to measure the decrease in C_p with pressure up to 1.6 kbar for polyethylene, but found that the decrease was within the experimental accuracy of the measurements and could not be determined. According to eq. (14), the decrease should be 1.6% in this case, which is about what Karl expected but was unable to measure.

HEAT CAPACITY RATIO

As mentioned in the Introduction, the ratio of the heat capacities is needed to convert an adiabatic bulk modulus to an isothermal value. This ratio, $C_p/C_v \equiv \gamma$, is generally found to be larger in polymers than in metals and larger in polymer melts than in polymer solids, though data of this type is scarce. The ratio can be calculated from the identity

$$1/\gamma = 1 - (C_p - C_v)/C_p \quad (15)$$

Thus, to calculate γ , we need not only $C_p - C_v$ as calculated above from the PVT equation of state, but also the value of C_p which would require a PVTS equation of state. In this paper, experimental values of $C_p(0, T)$ from the literature⁸ will be used.

The temperature dependence of γ , at zero pressure, calculated using eq. (15) is shown in Figure 6 for several polymers. C_p/C_v has a maximum value as does $C_p - C_v$ (Fig. 1). For C_p/C_v , however, a reduced variable plot does not produce a master curve since $C_p(0, T)$ is not a universal function of T/T_0 .

In an earlier study of the heat capacity ratio⁹ that included polymer melts as well as solids, values of the same magnitude as Figure 6 were found. The literature data used in that empirical correlation, however, was not extensive enough to show the peak in γ predicted here.

APPROXIMATE RELATIONS

Since reliable thermodynamic data for calculating heat capacity relations is often not available, various approximate relations are useful. One such relation is the Nernst-Lindemann equation.¹⁰ They showed that for metals below their melting point, the temperature dependence of $C_p - C_v$ at zero pressure is given by

$$C_p - C_v = C_p^2 TA \quad (16)$$

where A is a constant (with units of mol/J) for each metal. This result follows from eq. (1) assuming that $\alpha \sim C_p$ (from the Gruneisen equation of state) and that VB_T is a constant. Nernst and Lindemann further showed that

$$C_p - C_v = C_p^2 (T/T_m) A_0 \quad (17)$$

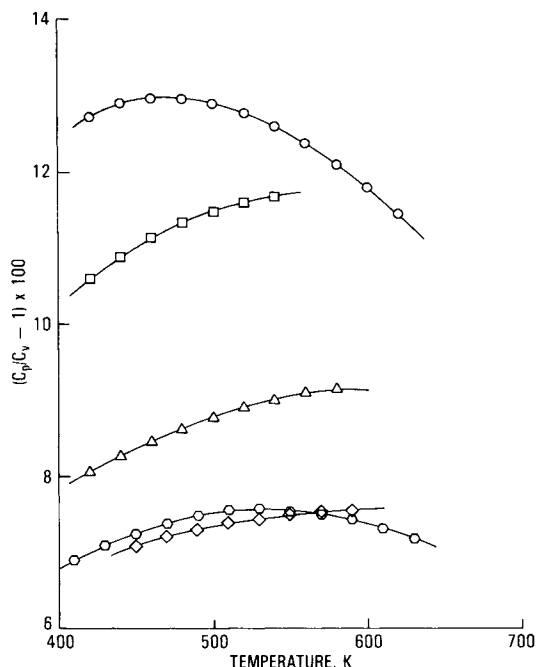


Fig. 6. Heat capacity ratio vs. temperature: (○) polyethylene; (□) poly(methylmethacrylate); (△) polystyrene; (◇) polypropylene; (◇) polybutene⁻¹.

where A_0 is now a universal constant (with units of mol K/J). These equations have been applied to solid polymers¹¹⁻¹³ and provide useful estimates when data is not available. The relation tends to be less accurate at higher temperatures.

In attempting to apply the above equations to polymer melts, poor correlation is found. For example, the A value for polyethylene changes by a factor of 2 over the temperature range from 420 to 630 K. Also, the A_0 values for polyethylene at 420 K and polypropylene at 600 K differ by an order of magnitude.

An improvement to the Nernst-Lindemann equation can be obtained by noting that, for polymer melts, $\alpha \sim T^{1/2}$ (from the equation of state) and $C_p \sim T$ (from experiment⁸) so that $\alpha^2 \sim C_p$, in contrast to the Nernst-Lindemann¹⁰ assumption. It would then follow that

$$C_p - C_v = C_p T A' \quad (18)$$

and, in fact, A' is more nearly constant than is A . Even better results are found using the empirical observation that

$$C_p - C_v = C_p A'' \quad (19)$$

In this case, for polyethylene, $A'' = 0.107$ and varies by only $\pm 6\%$ over the temperature range from 420 to 630 K. For polybutene-1, the variation is less than $\pm 2\%$. Remembering that $C_p - C_v \sim T^2 \exp(-4\bar{T}^{3/2})$ and $C_p \sim T$, one would not expect $(C_p - C_v)/C_p$ to be constant over a wide tem-

perature range, but, over the experimental range measured, this appears to be a useful approximation.

Another approximate relation examined involves the combination of reducing parameters RT_0/B_0V_0 that appears in the definition of reduced heat capacity. For polymer solids, RT_0/B_0V_0 is approximately a constant for crystalline polymers and also for amorphous polymers.¹⁴ For all 23 polymer melts for which reducing constants are available,¹ the average value of RT_0/B_0V_0 is 4.47 g/mol, with no difference between crystalline and amorphous polymers. Most polymers have values within $\pm 20\%$ of the average. This value is intermediate between the values found for solid crystalline (4.21 g/mol) and solid amorphous (5.41 g/mol) polymers. While crude, this relation is very useful in those cases where PVT data is not available. In particular, if only $P = 0$ data is available, one can calculate V_0 and T_0 from $\ln \bar{V} = \bar{T}^{3/2}$ and estimate B_0 . In this way, pressure dependence can be estimated from temperature dependence.

One final approximation was investigated. It has been shown¹⁴ that, for amorphous polymers below the glass transition, there is a correlation between T_0 and T_g . For these same amorphous polymers above the glass transition, however, no correlation was found.

SUMMARY AND CONCLUSIONS

A new PVT equation of state was used to calculate the temperature and pressure dependence of $C_p - C_v$ for polymer melts. The results are in the form of universal master curves in terms of reduced variables. As a function of temperature, $C_p - C_v$ increases to a peak value and then decreases. For many polymers, degradation occurs before the peak temperature is reached, but for polydimethylsiloxane the peak is predicted to occur at 480 K and should be measurable. As a function of pressure, $C_p - C_v$ has a shallow minimum. Typically, there is a 2% change in going from 0 to 2 kbar so that this effect is difficult to measure.

The PVT equation of state was supplemented with experimental $C_p(T)$ data from the literature in order to calculate C_p/C_v . Again, as a function of temperature, a peak was found.

In those cases where complete PVT data are not available, an approximation related to the Nernst-Lindemann equation was found to be useful. Also, the combination of reducing parameters RT_0/B_0V_0 was found to be approximately constant. This allows, for example, pressure dependence to be estimated from temperature dependence.

These results demonstrate the usefulness of the simple, analytic equation of state derived earlier to correlate PVT measurements and to extract the temperature and pressure dependence of the derivatives of that data needed to calculate $C_p - C_v$ and C_p/C_v .

This work was supported by the Center's Independent Research Program.

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Received June 12, 1985

Accepted August 5, 1985