

On the Applicability of the Lennard-Jones Potential Function to Amorphous High Polymers

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SYNOPSIS

Pressure–volume–temperature measurements were performed on five amorphous thermoplastics. From these data, first derivatives of internal energy with respect to volume were calculated. These derivatives were cast into the Lennard-Jones form and the two defining parameters were evaluated for each polymer. It was found that, when the polymer is in the glassy state, these parameters correspond to the volume and internal energy of the polymer at absolute zero. For melts, the first derivatives are constant within the accuracy of these experiments regardless of temperature, pressure, or volume. As a result, the Lennard-Jones potential was found to be a good model for the amorphous glassy state and inappropriate above T_g . © 1993 John Wiley & Sons, Inc.

INTRODUCTION

As exemplified in Ref. 1, a great deal of effort has been expended over the last few years in developing computational codes for the prediction of polymer properties from the molecular structure alone. By using five “primary” parameters, Seitz² was able to predict an astonishing number of properties via group contribution methods. Included in the predictive methods are fundamental thermodynamic relationships that require a knowledge of the potential energy function for a polymer. The relationship of choice has, so far, been the Lennard-Jones (L-J) function.³ Other potential energy functions might have been used. The classical Morse function⁴ is one example. An attempt to use this alternative function resulted in similar values for volume and energy parameters. Since it made no difference for the purposes of this paper, the L-J function was chosen as representative of other possible functions. Both the L-J and Morse functions define a zero-point state by accounting for both attractive and repulsive components of interaction. Other functions such as the London equation⁵ typically ignore the repulsive portion of the potential function and, consequently, do not define a stable zero-point state. The L-J relationship, as well as the others, was orig-

inally derived for small molecule systems and there is no *a priori* reason for being able to apply it to polymeric systems. I felt that it was necessary to either establish the validity of the model or present a better alternative. It was the purpose of this article to demonstrate the utility of the L-J and also to interpret the values of the parameters used in the equation.

THEORY

Thermodynamics

The original form of the L-J potential is³

$$U(r) = E_G \times \left[2 \times \left(\frac{r_G}{r} \right)^6 - \left(\frac{r_G}{r} \right)^{12} \right] \quad (1a)$$

where r_G is the molecular spacing at the potential well minimum and E_G is the depth of the potential well (see Fig. 1). The subscript “0” is normally used with the L-J parameters, but we will be using it to refer to the experimentally evaluated volume and energy at absolute zero. In its place we chose to use the subscript “G” for the values obtained by fitting pressure–volume–temperature (PVT) data to the L-J function. Seitz² found it more useful to cast the function in terms of volume, using V_G as the spatial parameter:

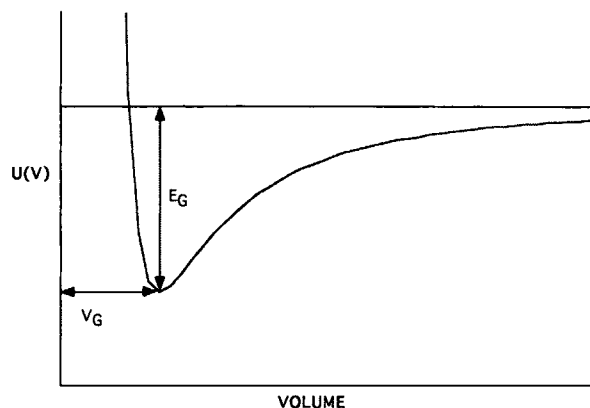


Figure 1 The L-J potential function from eq. 1 (b).

$$U(V) = E_G \times \left[2 \times \left(\frac{V_G}{V} \right)^2 - \left(\frac{V_G}{V} \right)^4 \right] \quad (1b)$$

I will continue to use this latter form for convenience. Actually, I will more frequently use the first derivative:

$$\frac{dU(V)}{dV} = \frac{4 \times E_G}{V} \times \left[\left(\frac{V_G}{V} \right)^2 - \left(\frac{V_G}{V} \right)^4 \right] \quad (2)$$

The use of the first-derivative results from the relationships given by Kaeble (Ref. 6, p. 254):

$$\left(\frac{\delta U}{\delta V} \right)_T = T \left(\frac{\delta P}{\delta T} \right)_V - P \quad (3)$$

$(\delta P / \delta T)_V$ is easily evaluated as follows:

$$\left(\frac{\delta P}{\delta T} \right)_V = - \left(\frac{\delta V}{\delta T} \right)_P / \left(\frac{\delta V}{\delta P} \right)_T = \beta \times B \quad (4)$$

where β is the volumetric thermal expansion coefficient, and B , the bulk modulus. Both values are available from PVT data. The derivative then becomes the primary value from which the parameters E_0 and V_0 are evaluated.

Specific Heat Relation to Thermal Expansion

One value that is employed in this work is the specific volume of a polymer at absolute zero. Some data are available in the literature⁷ that are broad enough to allow extrapolation to zero and these were used where appropriate. However, expansion data for most of the polymers studied were not available and a new technique was tried (see Experimental

section), which, by itself, was not as precise as needed. Therefore, a relationship between specific heat and expansion⁸ was used to improve the precision:

$$\frac{V_T - V_0}{V_T} = \frac{I_T}{Q_0 - k \times I_T} \quad (5)$$

where V_T is the volume at temperature T , and I_T is the integral of heat capacity at constant volume (C_v) with respect to T . Q_0 and k are fitting constants. Reference 8 uses the integral of heat capacity, which is a molar quantity, but for reasons given below, specific heat that is based on a unit mass was used in this work.

EXPERIMENTAL

Materials

A total of five polymers were investigated. These were (abbreviation in parentheses)

1. Polystyrene, Styron* 685D (PS).
2. Styrene acrylonitrile copolymer, Tyril* 880 (TY).
3. Polycarbonate, Calibre* 300-10 (PC).
4. Phenoxy resin, PKCG† (PHEN).
5. Poly(methyl methacrylate), Plexiglas‡ (PMMA).

PVT Measurements

PVT data on the above five materials were obtained using a Gnomix™ bellows-type dilatometer. Specific volumes were measured at 10 MPa and 5 K increments over ranges from 0.1 to 200 MPa and from 300 K to an upper limit that depended on the thermal stability of the polymer. An example of the data is shown in Figure 2.

Materials were aged for 4 h at 20 K below their glass transitions before measuring PVT properties. We have found that this procedure reduces physical aging effects to a negligible level. All absolute volume data rely on an accurate value of density at some reference point. The density of each sample was measured at room temperature via a buoyancy technique to 0.1%.

* Trademark of The Dow Chemical Company.

† Trademark of Union Carbide.

‡ Trademark of Rohm and Haas.

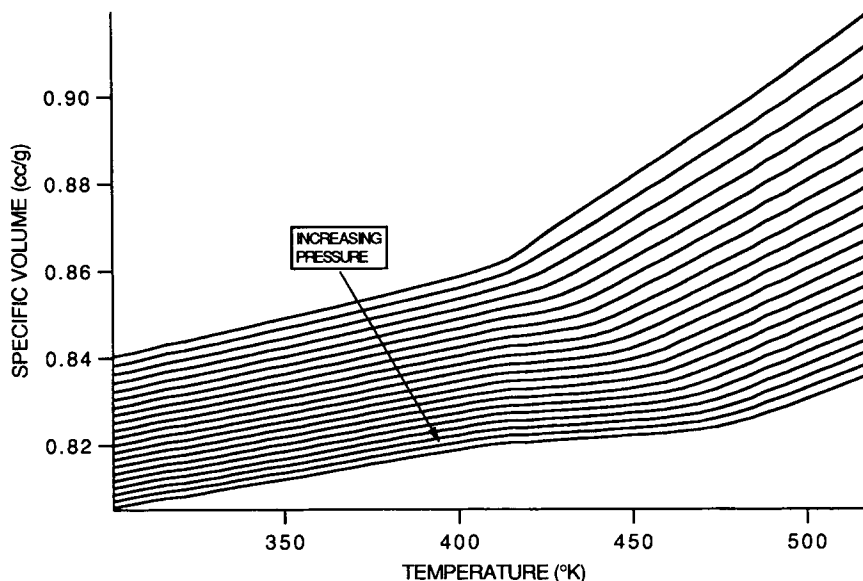


Figure 2 Primary PVT data for annealed PC.

Specific Heats

Heat capacities at constant pressure (C_p) were obtained by Prof. E. Westrum of the University of Michigan using adiabatic calorimetry. These data were converted to specific heat and then compared with the data from Ref. 7 for PS. The results are shown in Figure 3. Actually, the heat capacity referred to in eq. (5) is C_v (i.e., the heat capacity at constant volume). In most cases, the difference be-

tween C_p and C_v is negligible, but values for C_v were obtained from⁹

$$C_v = C_p - V \times T \times \beta^2 \times B \quad (6)$$

Cryogenic Thermal Expansion

The usual technique for measuring thermal expansion at cryogenic temperatures is via a quartz dilatometer with liquid helium as a refrigerant.⁵ In the

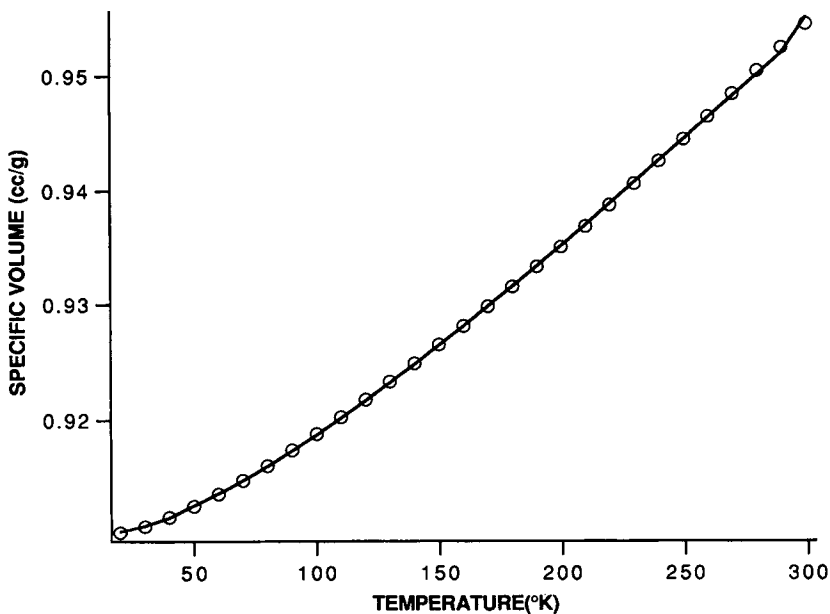


Figure 3 Correlation between (solid line) specific heat and (open circles) volume from Ref. 5 based on eq. (5).

absence of such a dilatometer and because of the availability of a Janis model 350-HT helium refrigerator, an alternative technique was tried. A low-temperature cell with viewing windows was obtained and width measurements on a 20×6 mm film sample were accomplished using a laser micrometer that has a precision of $0.5 \mu\text{m}$ (LasermikeTM Model 501). Typical results are shown in Figure 4 for annealed PC. It is suspected that the primary sources of error in this technique are distortion in the cryogenic cell coupled with internal reflections of the laser beam between the cell windows. An improved version is currently being tested. Comparisons were made for both PS and PC with the data from Ref. 7 with good agreement. It is felt that the combination of laser measurements with the extrapolation provided by eq. (5) gives credible values for the specific volume at absolute zero (V_0).

RESULTS

Specific Heat

Figure 5 presents specific heat data for all the materials. Up to 50 K, the five polymers have similar heats. Between 50 and 150 K, PMMA separates itself from the others. In the vicinity of 150 K, the phenoxy resin shows an increase relative to the remaining thermoplastics. It rises until a value similar to PMMA is reached around 300 K. When converted to heat capacities, data for PMMA and PS show excellent agreement with the literature data.^{10,11}

Thermodynamic Analysis and the Lennard-Jones Function

Thermal expansion coefficients and bulk moduli were evaluated from finite differences in the original PVT data. These along with the temperature and pressure are all the data needed to determine the first derivative of the internal energy $(\delta U/\delta V)_T$ as shown in eqs. (3) and (4). Figure 6 shows a typical set of converted data. Each line in Figure 6 refers to a different pressure. In the glass transition regions, the upper lines correspond to low pressures, while the lower lines correspond to high pressures. Actually, the derivative values relate better to the volume as shown in Figure 7. Beyond the transition region, the energy derivatives are essentially constant.

We will now look at the values below T_g that are shown in Figure 7 as a function of specific volume. It should not matter how one gets to a certain volume state (i.e., temperature and pressure combining to give a particular volume) if the L-J function is to be useful, and this is indeed the case. In Figure 7 we have plotted all data regardless of the temperature and pressure needed to reach a particular value of specific volume. A fit to the first derivative of the L-J function is shown. Also given are the two L-J parameters that were obtained by fitting the data to eq. (2). All the parameters obtained by the fitting process are listed in Table I along with the measured values of specific volumes and cohesive energies at absolute zero. These latter values were obtained by

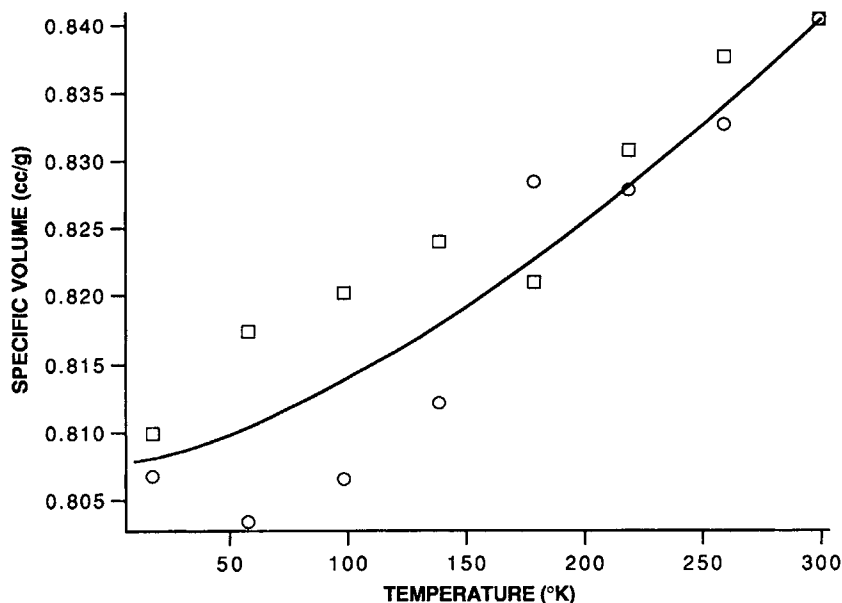


Figure 4 Specific volume of annealed PC from laser micrometer measurements (symbols ○ and □) showing fit to specific heat data (solid line).

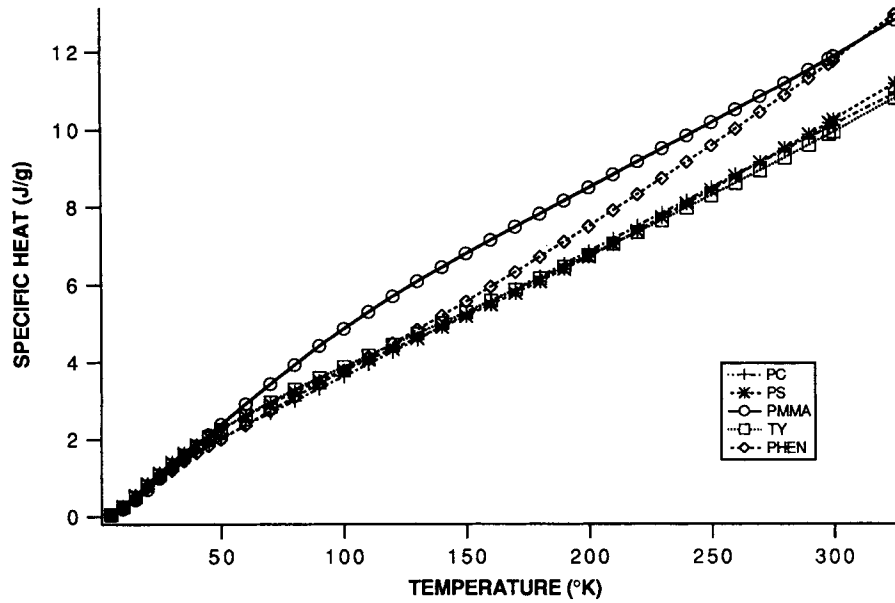


Figure 5 Specific heats.

adding the temperature integral of specific heat to the standard (298 K) cohesive energy.²

These data are also shown in Figures 8 and 9. Excellent agreement is seen when comparing the volume parameter (V_G) with zero-temperature volume (V_0) in Figure 8. In Figure 9, we compare the energy parameter (E_G) evaluated from fitting the L-J function with the internal energy at absolute zero (E_0).

Pressure-Volume-Temperature

Figure 2 shows the well-known pressure effect on volume just above T_g ¹² (i.e., there exists a wedge-shaped temperature range just above T_g at elevated pressures where the specific volume remains nearly constant with increasing temperature). This article is primarily concerned with the glassy state, but a future article will discuss the melt region in detail.

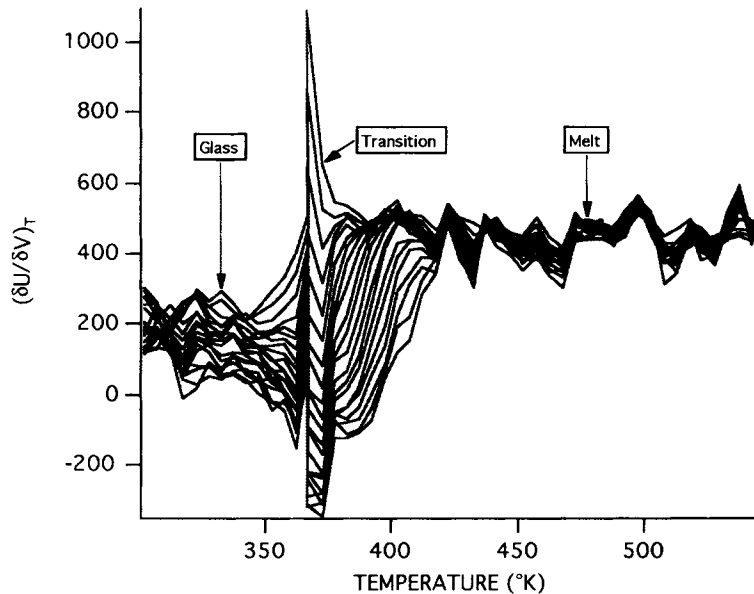


Figure 6 $(\delta U/\delta V)_T$ for phenoxy resin.

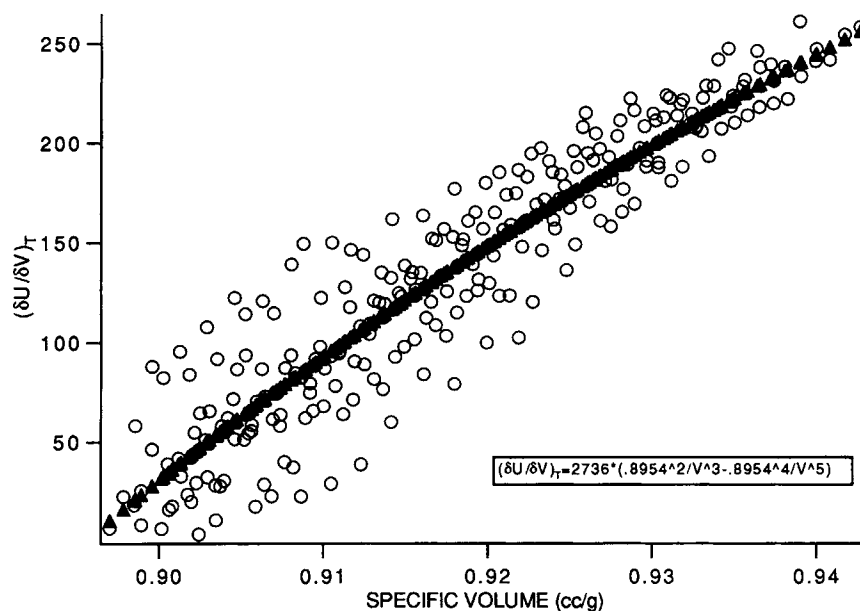


Figure 7 $(\delta U/\delta V)_T$ for Tyril™ glass (open circles) with fit to eq. 2 (filled triangles).

As for the transition region, Quach and Simha¹³ said that it is the result of rate effects and aging. Zoller and Hoehn¹⁴ described the phenomenon as resulting from “a series of different glasses” that arise during the experimental procedure. We cannot support or dispute these assertions based on the data at hand.

DISCUSSION

Thermodynamic Analysis and the Lennard-Jones Function

As scattered as the data plotted in Figure 7 are, they do seem to support the one basic assumption, i.e., it does not matter what combination of temperature and pressure we use to arrive at a particular volume—the potential energy state is the same. The

large scatter seen is most likely because we are dealing with small differences of large numbers in calculating the material properties. Most of the scatter seems to arise in the thermal expansion values, which should not be too surprising since the thermal expansion is not as sensitive as is the bulk modulus to changing conditions. For example, PS shows thermal expansion coefficients increasing by 40%, while the bulk modulus is decreasing by 70% as the volume increases by 6% in the glassy state. One attempt to fit the data with polynomials to reduce the scatter actually appeared to make things worse by introducing artifacts at the pressure extremes.

Perhaps the most gratifying result of this work is the realization that V_0 and V_G as well as E_0 and E_G are nearly the same. In other words, the volume and energy parameters in the L-J equation essentially describe the state that the sample would reach at absolute zero. It may be that more accurate measurements and/or more careful annealing could bring the measurements into closer agreement, but for this initial paper the conclusion seems reasonable.

The description of $(\delta U/\delta V)_T$ given by L-J is entirely consistent with the observed values. Therefore, the L-J function does form a satisfactory relationship for predictive purposes in the glassy state, as in Ref. 2.

Although it is possible to use the L-J potential to describe the energy state of glassy polymers, it does not hold true for states above T_g . In the melt, we see that $(\delta U/\delta V)_T$ does not seem to have any

Table I Materials and Parameters

Polymer	E_0 (J/g)	E_G (J/g)	V_0 (cc/g)	V_G (cc/g)
PC	563	563	0.8071	0.7970
PS	608	562	0.9097	0.9065
PMMA	526	764	0.8169	0.8155
TY	653	684	0.8943	0.8954
PHEN	719	636	0.8328	0.8139

E_0 and V_0 are the cohesive energy and specific volume at absolute zero, respectively. E_G and V_G are the energy and volume parameters from fitting the potential energy function, respectively.

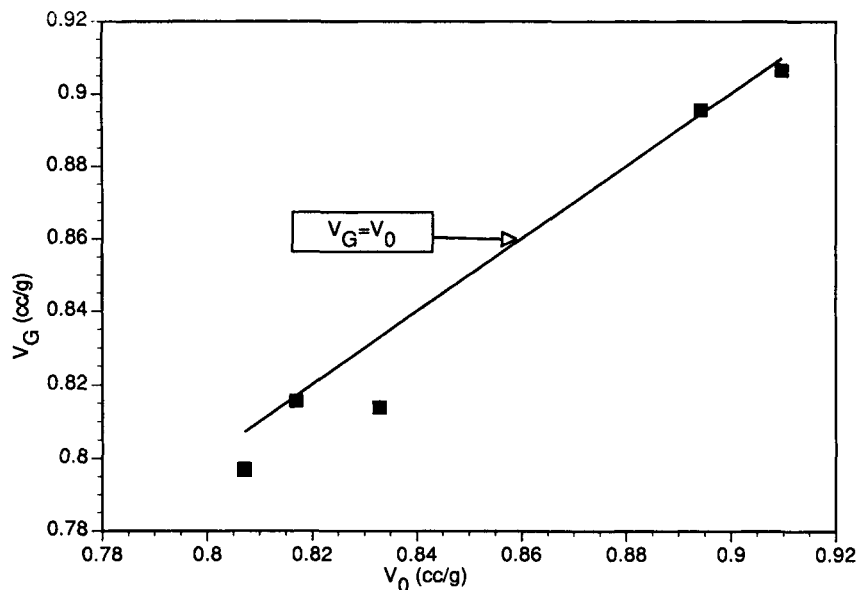


Figure 8 Comparison of the volume parameter (V_G) from eq. 2 with the volume at 0 K (V_0).

correlation with volume; it may even be constant. Hence, it cannot follow a similar potential function. In the transition zone between glass and melt, neither relationship (L-J nor constant derivative) holds.

CONCLUSIONS

Pressure-volume-temperature measurements provide a convenient method for evaluating thermo-

dynamic pressure functions for high polymers. The values obtained from these measurements indicate that the L-J potential energy function is a reasonable model to use for prediction of polymeric material properties in the glassy state. This seems especially true since we have found that the constant parameters in the equation have physical meaning, i.e., they are the volume and cohesive energy at absolute zero. However, the L-J function is inappropriate to

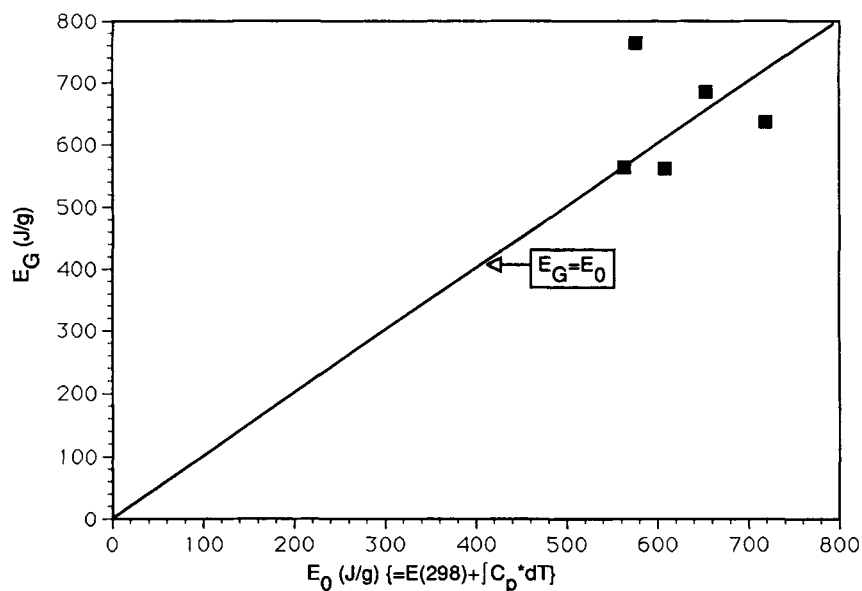


Figure 9 Comparison of the energy parameter (E_G) from eq. (2) with the cohesive energy at 0 K (E_0).

use above the glass transition temperature since the energy derivative for the melt is nearly constant for all conditions of temperature, pressure, and volume. In the transition zone, neither potential applies.

We have had some success using a laser micrometer and helium refrigerator to measure the contraction of samples at very low temperatures. However, it was necessary to back these readings with specific heat measurements to achieve credible values for the densities at absolute zero.

The following contributions to this work are gratefully acknowledged. Heat capacities were measured by Prof. E. Westrum of the University of Michigan. PVT data were obtained from S. Humphrey of the Analytical Laboratory of the Dow Chemical Company. Room-temperature density measurements were performed by C. Brown. A computer code for converting the raw data into usable numbers was written by E. Eidsmoe. I appreciate the many discussions with J. Seitz and J. Bicerano. The cooperation of D. Moll and D. Hayes in using their helium refrigerator is also appreciated. All those who are acknowledged, except Prof. Westrum, are of the Dow Chemical Co., Midland, MI.

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