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Notes

Theoretical Equation of State: Some Scaled Relationships

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1. Introduction

In a recent paper Sanchez, Cho, and Chen[1] discuss compression data of amorphous polymers, their solutions, and an organic liquid over a range of temperatures and pressures. The choice of a reduced pressure quantity ($p - p_0/B_0$, with B_0 the bulk modulus at a reference pressure p_0, results in a single, temperature-independent relation between the corresponding volume quantity ($\ln(V/V_0)$ and B/B_0 respectively as functions of the above quantity. The authors then specify on thermodynamic grounds conditions to be satisfied by the configurational free energy. Moreover, they raise the question whether molecular theories, although satisfying a principle of corresponding states, are able to describe their scaled relationships.

The purpose of this paper is to examine the above results in the frame of our hole theory. Before doing this, however, we point to a recent derivation of an isothermal equation of state[2] which explicitly exhibits a single relation between volume ratio and p/B_0 independent of temperature. The hole theory of Simha and Somcynsky (SS) however requires evaluation of derivatives with due consideration of the V- and T-dependent hole fraction h, derived from free energy minimization.

2. Development

Jain and Simha[3] derived the formal scaled expressions for the thermal expansivity and the compressibility in the SS theory. Another concern, pertinent for the present intentions, was the relation between the theoretical equation of state and the quite successful empirical Tait equation, viz.

$$V(P,T)/V(0,T) = 1 - C\ln[1 + p/B(T)] \qquad (1)$$

The noteworthy points in eq 1 are the practical universality of the C parameter derived for polymer melts and glasses and the pressure independence of the function $B(T)$. Under these conditions, it will be noted, the Tait equation is consistent with the universal relationships under discussion.

However, we have to deal now with the results of the hole theory. For reasons to be justified below, it will be helpful to proceed with the results of a theoretical analysis of the Tait relation (1). The basic connection is generated by the defining equations[4]

$$V(0,T)C = -(\partial p/\partial V)_T/(\partial^2 p/\partial V^2)_T$$

$$B(T) = (\partial p/\partial V)_T^{\,2}/(\partial^2 p/\partial V^2)_T - p \qquad (2)$$

Jain and Simha[3] evaluated the derivatives on the right-hand side of eq 2 and obtained explicit expressions for the two Tait parameters, consistent with the SS theory. It turns out (see below) that the Tait B is not a pure temperature function and C is not strictly constant. However, once these two Tait functions are known, we obtain the bulk modulus:

$$B = -V(\partial p/\partial V)_T = \frac{V(T,p)}{V(T,0)}[B(T,P) + p]/C(p,T) \qquad (3)$$

with the volume ratio given by eq 1 and a corresponding expression for the bulk modulus B_0 at zero or at another reference pressure. The reduced pressure quantity p/B_0 can then be written as

$$\tilde{p}C(0,\tilde{T})/\tilde{B}(0,\tilde{T}) \qquad (4)$$

where the tildes indicate scaled quantities.

Now the results emanating from the SS theory could be expressed by the following scaled interpolation expressions:[3]

$$\tilde{B}(\tilde{p},\tilde{T}) = 0.5470\exp(-31.73\tilde{T}) + \tilde{p}(0.17091 - 9.2494\tilde{T} + 73.589\tilde{T}^2) \qquad (5)$$

$$C(\tilde{p},\tilde{T}) = 0.06012 + 0.9192\tilde{T} + \tilde{p}(0.03952 - 1.6188\tilde{T})$$

The limits of validity are given as

$$0.031 \le \tilde{T} \le 0.051; \qquad 0.027 \le \tilde{p} \le 0.32$$

The deviations between these and the actual expressions in $\tilde{B}(\tilde{p},\tilde{T})$ increase from 0.2% at the lower limit to 1% at the upper limit of pressure. For $B(0,\tilde{T})$ the maximum departure is 2.5%. Considering the usual values for scaling temperature T^* and scaling pressure p^* of the order of 10^4 K and over 500 MPa, respectively, the state limits are adequate.

3. Results

As illustrations we consider two polymer melts with equations of state previously determined up to pressures of ca. 200 MPa, namely, polystyrene[5] and *n*-butyl methacrylate,[6] and analyzed in terms of the theory. We employ the scaling parameters V^*, T^* and P^* presented in these references. Improved numerical procedures in the superposition of experimental and scaled theoretical equation of state surfaces[7] have generated somewhat different values of these parameters and improved agreement between experiment and prediction. However, for our purposes the original values are adequate.

Figure 1 shows some of the computations. The results for the two polymers are superimposed and two reference pressures are employed. A universal relation over the range of temperatures exhibited ensues. The identical conclusion as for the volume ratio V/V_0 is reached in Figure 2 in respect to the modulus ratio B/B_0, where two different pressures are employed.

It is obvious then to consider the general scaled relationships. In Figure 3 the volume ratio is exhibited with zero scaled pressure as the reference state. We observe departures from the curve defined by the lower temperatures at the higher temperatures and pressures.

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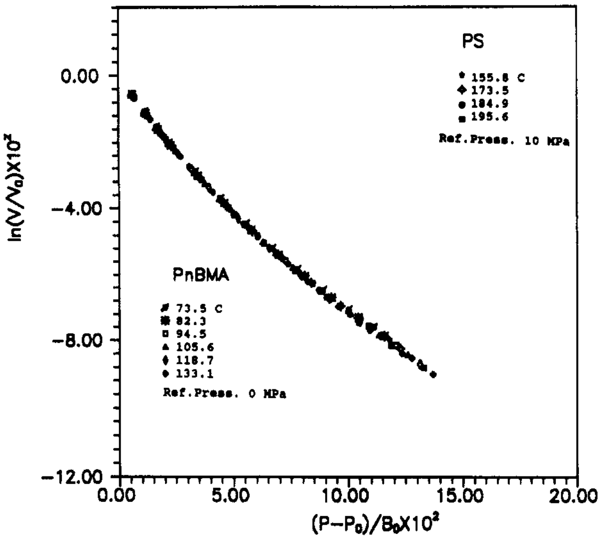

Figure 1. Computed volume ratio V/V_0 as a function of the reduced pressure quantity $(p-p_0)/B_0$ for polystyrene and *n*-butyl methacrylate, with different reference pressures, p_0.

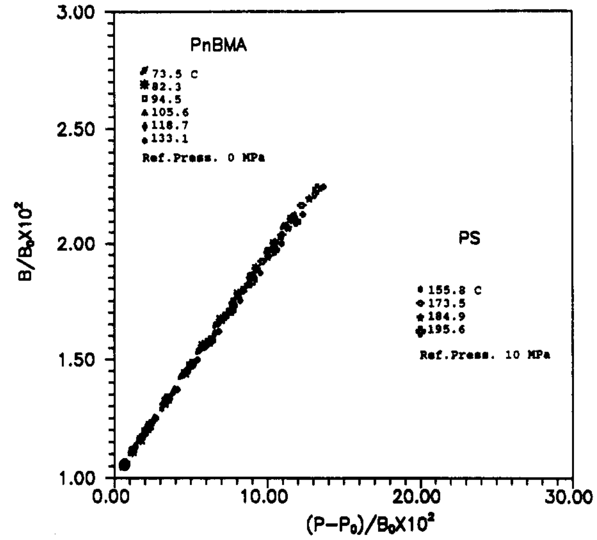

Figure 2. Computed ratio B/B_0 of compression moduli as a function of the reduced pressure quantity $(p - p_0)/B_0$ for polystyrene and *n*-butyl methacrylate, with different reference pressures.

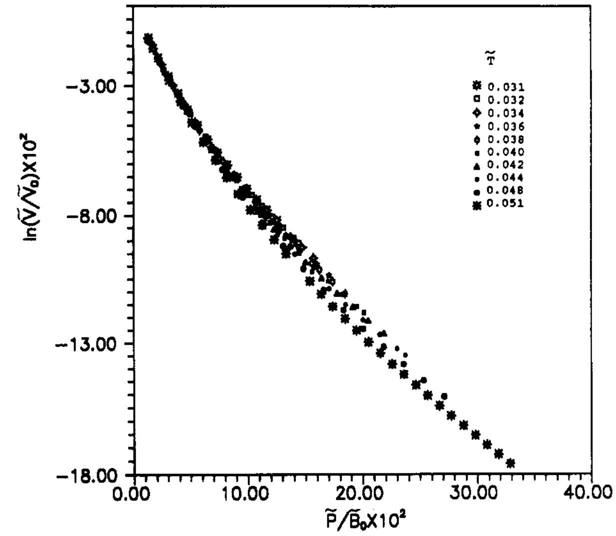

Figure 3. General computed volume ratio as a function of the reduced pressure quantity, all expressed in the scaled variables of the hole theory.

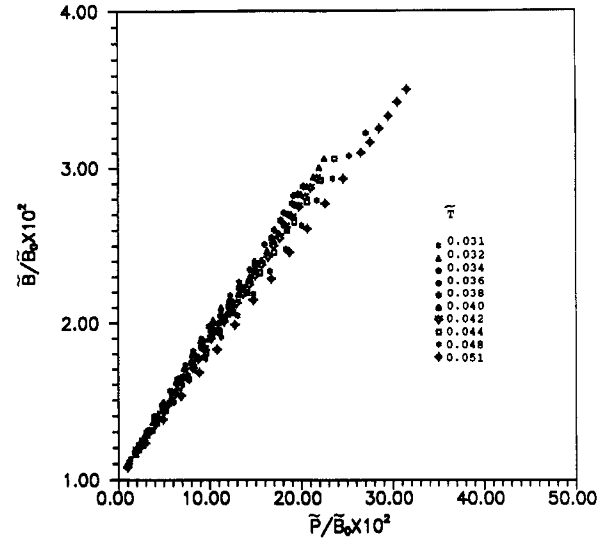

Figure 4. General computed ratio B/B_0 as a function of the reduced pressure quantity, all expressed in the scaled variables of the hole theory.

The maximum $\tilde{T} = 0.051$ corresponds for polystyrene to a temperature of ca. 650 K and of 510 K for *n*-butyl methacrylate, i.e., far above the physically reasonable range. The trend seen in Figure 3 and consistently in Figure 4 with increasing $\tilde{T}$ is in accord with an earlier observation[8] of a slow increase of the scaling temperature T^* with increasing T. We finally note that the deviations inherent in eq 5 are too small to account for the effects seen in Figures 3 and 4.

4. Discussion

We conclude that the SS theory yields the temperature-independent relations involving the compression of amorphous polymers above T_g. In ref 1 an example of a polymer solution is also cited. The hole theory in the SS formulation has been generalized to multiconstituent systems[9] and compared with experiment on low molar mass mixtures,[9] polymer solutions,[10] and polymer mixture.[11] The theory yields formally the identical scaled equation of state as for a single constituent, with the scaling parameters explicit functions of composition. Thus the same picture as seen in Figures 3 and 4 emerges, i.e., superposition for different temperatures and compositions.

A final point concerns glasses. For different formation histories the Tait eq 1 has been shown to be an adequate representation of experimental data.[5,6,12] The differences between different systems are all expressed by the Tait B, with the universality of C extended from the liquid state. Hence one may conclude that a reasonable consistency with universal compression results continues in the glassy state.

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References and Notes

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