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Theoretical Equation of State: Thermal Expansivity, Compressibility, and the Tait Relation

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ABSTRACT: Exact scaled expressions for the thermal expansivity α and the isothermal compressibility β are derived as functions of temperature and pressure. In the frame of the hole theory, α at atmospheric pressure has been frequently obtained as the derivative of an approximation to the exact volume–temperature function. Differences are seen, and an improved approximation is now extracted from the rigorous expression, which reduces the previous temperature dependence of α. Summaries of *PVT* measurements at elevated pressures and comparisons with theory are frequently presented in terms of the Tait equation. We derive formal expressions for the quantities *C* and *B* and observe variations of the "constant" *C* with pressure and temperature and a dependence of the temperature function *B* on pressure. These variations, even if numerically small in certain ranges of temperature and pressure, are significant for a computation of β or of bulk moduli. Accurate approximations to the theoretical *C* and *B* functions over specified ranges of the scaled variables are given. When substituted into the Tait expression for β, the results are numerically consistent with the analytical equations. They are computationally convenient and are recommended for the discussion of compressibilities and bulk moduli. The exact scaled expressions remain valid for multiconstituent systems.

Introduction

In recent times explicit equations of state (*PVT*), with emphasis on chain-molecular fluids, have been developed by a series of authors.[1-5] Moreover, comparisons between these theories in numerical[6-8] or analytical terms[9] have been presented.

Numerous studies of single-constituent and multiconstituent melts, the latter either as physical mixtures[10] or as copolymers,[11,12] have served to illustrate the quantitative success of the hole theory developed in ref 5 (SS). The configurational thermodynamic functions appear in scaled form, and the combination of experimental and scaled theoretical *PVT* surfaces then yields the scaling pressure P^*, temperature T^*, and volume V^* as characteristic *constants* of the particular system. This, of course, implies an adequate representation of the experimental data by the theoretical expressions.

The purpose of this paper is not the comparison of SS with other theories, sufficiently clarified by other authors, nor, for that matter, the relation to experiment, already explored extensively. However, two aspects merit further attention in the frame of the SS theory. Both have a bearing on the numerical procedures used in the evaluation of experimental data in terms of theory. Both involve temperature and volume derivatives. Besides the intrinsic interest in these functions, they play a role in the evaluation of the scaling parameters. Two coupled equations, one of these in trancendental form, involve the reduced variables of state and the vacancy fraction. A numerical approximation to the scaled volume–temperature function at zero reduced pressure has been most frequently employed to obtain the characteristic volume and temperature parameters. This has obvious implications for the theoretical prediction of thermal expansivities. Second, experimental data at elevated pressures have frequently been expressed and then employed in terms of the empirical Tait relation to test theories. An interpretation of this equation based on our theory remains to be investigated.

In what follows we obtain first exact expressions for the thermal expansivity as a function of temperature and pressure. Second, the functional dependencies of the Tait parameters are derived. The results of these computations are compared with previous results in terms of thermal expansivity and isothermal compressibility. No explicit experimental results are involved, and a scaled representation of all equations will be sufficient.

Recapitulation of Basic Equations

The reduced equation of state is[5]

$$\tilde{P}\tilde{V}/\tilde{T} = (1 - Q)^{-1} + (2y/\tilde{T})(A\Phi - B)\Phi \qquad (1)$$

with $Q = 2^{-1/3}y(y\tilde{V})^{-1/3}$, $\Phi = (y\tilde{V})^{-2}$, $A = 1.011$, and $B = 1.2045$. The vacancy fraction $1 - y$ for an s-mer satisfies the minimum condition on the free energy, viz.

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$$(s/3c)[(s-1)/s + y^{-1}\ln(1-y)] = (y/6\tilde{T})(2B - 3A\Phi)\Phi + (Q - 1/3)(1-Q)^{-1} \quad (2)$$

To the "flexibility" parameter $3c/s$ a universal value of unity has been assigned in the past for polymer ($s \to \infty$) single-constituent melts. This results in an effective principle of corresponding states.[13] The specific assignment affects numerical values (see below) but not the general conclusions.

Thermal Expansivity

An excellent approximation to the coupled eq 1 and 2 at atmospheric pressure ($\tilde{P} \to 0$) is provided by the linear relation[14]

$$\ln \tilde{V} = A(s,c) + B(s,c)\tilde{T}^{3/2} \quad (3)$$

$A(s,c)$ and $B(s,c)$ are numerics. For $3c = s \to \infty$, the appropriate plot derived from eq 1 and 2 yields the least-squares values $A(s/c{=}3) = -0.10335$ and $B(s/c{=}3) = 23.834_5$ in the range $1.65 \le 10^2\tilde{T} \le 7.03$. Smaller ranges yield slightly different values.[15] Equation 3 implies an analogous linear relation in the actual variables V and T. Indeed, the representation of experimental data not only for organic polymers, oligomers, solvents, and mixtures of such but moreover for molten inorganic salts and their mixtures[16] is excellent. This in terms of just two constants, rather than the several polynomial coefficients often employed in the literature. Finally, acceptance of eq 3 and the corresponding representation of the unreduced data yield immediately V^* and T^*, thus avoiding in particular graphical shifting procedures. This then is followed by a determination of P^*. This *consecutive* determination of scaling parameters was first replaced by Nies et al. by a *simultaneous* derivation of all three parameters from the experimental PVT surface.[8] As subsequently shown,[17] this generates changes in the numerical values of P^*, V^*, T^* and an enhanced accuracy of theoretical predictions.

Equation 3 yields the thermal expansivity

$$\tilde{\alpha} = (1/\tilde{V})(\partial\tilde{V}/\partial\tilde{T})_{\tilde{P}\to 0} = {}^3\!/_2 B(s,c)\tilde{T}^{1/2} = 35.751_8\tilde{T}^{1/2} \quad (4)$$

where the last expression applies to the case $3c/s = 1$ and $B = 23.834_5$. It is of interest then to examine the adequacy of eq 3 for the derivative, eq 4, and to derive rigorous expressions for $\tilde{\alpha}$ at low and elevated pressures. For this purpose we transform α into

$$\alpha = -(1/V)(\partial P/\partial T)_V/(\partial P/\partial V)_T \quad (5)$$

with $T(\partial P/\partial T)_V = (\partial U/\partial V)_T + P$. We have for the internal energy[5]

$$-\tilde{U} = (y/2)(2B - A\Phi)\Phi$$

$$(\partial\tilde{U}/\partial\tilde{V})_{\tilde{T}} = {}^1\!/_2(2B - 3A\Phi)\Phi(\partial y/\partial\tilde{V})_{\tilde{T}} + (2y/\tilde{V})(B - A\Phi)\Phi$$

Equation A5 (Appendix) yields in combination with eq 1 $(\partial\tilde{P}/\partial\tilde{T})_{\tilde{V}}$. The volume coefficient of pressure is given by eq A3. Equation 5 then provides the final expression for $\tilde{\alpha}$, viz.

$$\tilde{\alpha} = \frac{(y/2\tilde{T})(2B - 3A\Phi)\Phi X + Z/(1-Q)}{\tilde{T}\{Z[\tilde{P}\tilde{V}/\tilde{T} + R/3 + (4y/\tilde{T})(2A\Phi - B)\Phi] - X^2\}} \quad (6)$$

with

$$R = Q(1-Q)^{-2}; \quad X = {}^2\!/_3R - (2y/\tilde{T})(3A\Phi - B)\Phi$$

$$Z = {}^4\!/_3R + (y/2\tilde{T})(9A\Phi - 2B)\Phi + (s/c)[y^{-1}\ln(1-y) + (1-y)^{-1}] \quad (7)$$

To compute $\tilde{\alpha}$ from eq 6, one solves first the coupled eq 1 and 2 for a set of isobars. For $\tilde{P} = 0$, the solutions for $\tilde{V}$, $\tilde{T}$, and y have been tabulated.[14] Figure 1 displays the temperature dependence of $\tilde{\alpha}$ for a series of isobars. In actual pressures, these exceed the range up to 200 MPa usually encountered in the area of amorphous polymers, since P^* is of the order of 1000 MPa. As suggested by eq 4, $\tilde{T}^{1/2}$ is selected as the abscissa, and for comparison the result of this equation is included. We note a reduced temperature dependence of the thermal expansivity. Actually, eq 4 was shown to exagerate this dependence,[14] even while the numerical discrepancies in α were below 10%. The differences between eq 6 and 4, however, are smaller than that. The solid line for the zero-pressure isobar represents the equation

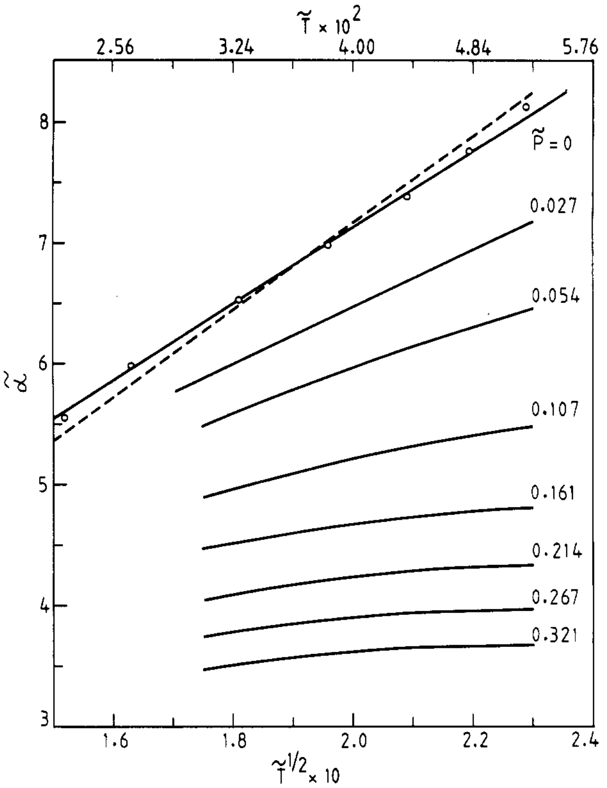

Figure 1. Scaled thermal expansivity $\tilde{\alpha}$ versus $\tilde{T}^{1/2}$: (---) eq 4; (—) eq 4′ for $\tilde{P} = 0$; ○, eq 6 with $\tilde{P} = 0$. Other lines, eq 6.

$$\tilde{\alpha} = 0.629 + 32.52\tilde{T}^{1/2}; \quad 2.3 \le 10^2\tilde{T} \le 5.2 \quad (4')$$

with deviations from the exact expression not exceeding 1%. Thus the temperature dependence of α is reduced by the appearance of the constant and the smaller value of the coefficient of $\tilde{T}^{1/2}$. With increasing pressure, the magnitude as well as the temperature dependence are reduced, and the approximate linearity in $\tilde{T}^{1/2}$ is lost at $\tilde{P} \simeq 0.05$ or $P \simeq 40$ MPa for polyethylene or polystyrene. Considering, however, that $\tilde{T}^{1/2} = 0.20$ corresponds to $T \simeq 500$ K for polystyrene, linearity still provides a useful estimate, particularly so at sufficiently low pressures.

Tait Relation and Compressibility

Experimental PVT measurements for organic polymer melts and glasses have frequently been summarized in terms of the Tait equation in the following form:

$$V(P,T)/V(0,T) = 1 - C\ln[1 + P/B(T)] \quad (8)$$

where $V(0,T)$ is the value at atmospheric (or a reference) pressure. A universal value, $C = 0.0894$, has been customarily employed, following the original analysis of hydrocarbons.[18] The temperature function B has been found to satisfy an exponential relation

$$B = B_0 \exp(-B_1 T) \quad (9)$$

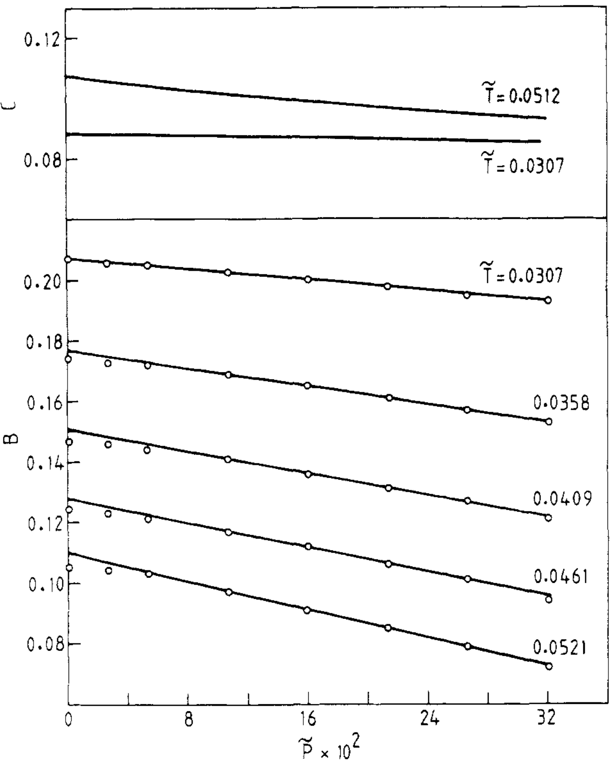

Figure 2. Tait parameter C (—) and function $\tilde{B}$ (O) as functions of $\tilde{P}$, eq 11 and 12. Lines for $\tilde{B}$ show approximate validity of linear relation.

The question of the connection between the Tait relation and the predictions of the cell theory was addressed some time ago.[19,20] This theory represents the limit of eq 1 for $y = 1$. A semitheoretical approach, based on the present theory, followed.[21] That is, the fixed value of C was *assumed*, and the scaled $\tilde{B}$ function derived. The result was indeed an exponential temperature dependence. We now reexamine the Tait relation consistently on the basis of current theory.

The starting point for all these analyses is the set of equations[20]

$$V(0,T)C = -(\partial P/\partial V)_T/(\partial^2 P/\partial V^2)_T;$$
$$B = (\partial P/\partial V)_T{}^2/(\partial^2 P/\partial V^2)_T - P \quad (10)$$

The cell theory analysis yields indeed a very slowly varying C, whereas $\tilde{B}$ varies much more rapidly.[20] However, the computations were carried out for the limit $\tilde{P} \to 0$ only, since the inadequacy of the PVT made further extensions unreliable. Casting eq 10 in reduced coordinates, we make use of eq A1–A9 and obtain

$$V(0,\tilde{T})C = \{\tilde{V}[\tilde{P}\tilde{V}/\tilde{T} + R/3 + (4y/\tilde{T})(2A\Phi - B)\Phi - X^2/Z]\}/\{2[\tilde{P}\tilde{V}/\tilde{T} + (2y/\tilde{T})(14A\Phi - 5B)\Phi + (R/9)(5 - 4Q)(1 - Q)^{-1}] + L\} \quad (11)$$

$$(\tilde{B} + \tilde{P})(\tilde{V}/\tilde{T}) = (1/\tilde{V})^2N^2/D \quad (12)$$

where N and D represent the numerator and denominator, respectively, in eq 11. Further definitions are

$$L = (X/Z)[S - 2X + (X/Z)(H + J + GX/Z)]$$

$$S = (2y/\tilde{T})(39A\Phi - 7B)\Phi - {}^4\!/_3R(1 - Q)^{-1}$$

$$G = (y/2\tilde{T})(27A\Phi - 2B)\Phi - {}^8\!/_9R(1 - Q)(1 - Q)^{-1} + (s/c)[y^{-1}\ln(1 - y) + (1 - 2y)(1 - y)^{-2}]$$

$$H = (4y/\tilde{T})(6A\Phi - B)\Phi - {}^2\!/_9R(1 - 5Q)(1 - Q)^{-1}$$

$$J = (2y/T)(15A\Phi - B)\Phi + {}^2\!/_9R(7 + Q)(1 - Q)^{-1}$$

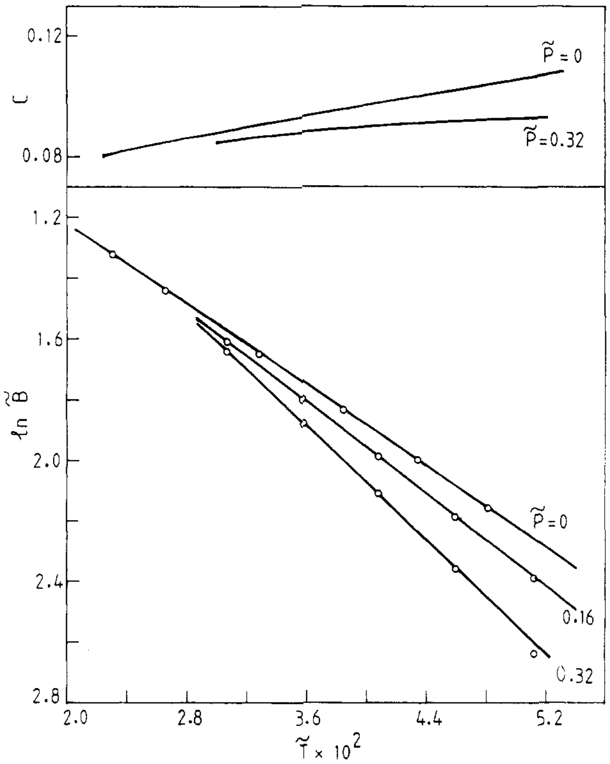

Figure 3. Tait parameter C (lines) and function $\tilde{B}$ (O) as functions of $\tilde{T}$, eq 11 and 12. Lines for $\tilde{B}$ show approximate validity of exponential dependence on $\tilde{T}$.

We observe that for $y = 1$ and $\tilde{P} = 0$, eq 11 and 12 reduce to eq 3 in ref 20. The results are shown in Figures 2 and 3 in the form of isotherms and isobars, respectively. In the former we observe a slow decrease of C, more pronounced at higher temperatures, with increasing pressure. $\tilde{B}$, on the other hand, varies more significantly with pressure at the higher temperatures. Figure 3 shows a variation of C, which is moderate over the range of temperatures usually occurring. For example, for polystyrene with $T^* = 12\,680$,[22] and $373 \leq T \leq 423$ K, C varies from about 0.089 to 0.095 and even less at the highest pressure shown, which corresponds to $P \simeq 240$ MPa. A semilogarithmic plot of $\tilde{B}$ results in a series of approximately linear isobars, in general accord with the empirical eq 9, but with a pressure-dependent slope and intercept. The results exhibited may be approximated by the following expressions:

$$\tilde{B}(\tilde{P},\tilde{T}) = B(0,\tilde{T}) + B_1(\tilde{T})\tilde{P}$$

$$\tilde{B}(0,\tilde{T}) = 0.5470 \exp(-31.73\tilde{T})$$

$$B_1(\tilde{T}) = 0.17091 - 9.2494\tilde{T} + 73.589\tilde{T}^2 \quad (12')$$

$$0.027 \leq \tilde{P} \leq 0.32; \quad 0.031 \leq \tilde{T} \leq 0.051$$

$$C(\tilde{P},\tilde{T}) = C(0,\tilde{T}) + C_1(\tilde{T})\tilde{P}; \quad 0.027 \leq \tilde{P} \leq 0.32$$

$$C(0,\tilde{T}) = 0.060\,12 + 0.9192\tilde{T}; \quad 0.023 \leq \tilde{T} \leq 0.052 \quad (11')$$

$$C_1(\tilde{T}) = 0.039\,52 - 1.6188\tilde{T}; \quad 0.031 \leq \tilde{T} \leq 0.051$$

These expressions provide computationally convenient approximations. The maximum deviation in $\tilde{B}(\tilde{P},\tilde{T})$ amounts to 0.2% at the lower limit, increasing to 1% at the upper limit of $\tilde{T}$. For $\tilde{B}(0,\tilde{T})$ the maximum departure is 2.5%. A decrease to 0.2% results from a change of the coefficients to 0.5740 and 33.26, respectively.

Clearly, any numerical agreement of the Tait relation, eq 8, with the theoretical equation of state rests on a

Table I
Scaled Compressibilities $10\tilde{\beta}$[a]

	$\tilde{T} = 0.0307$		$\tilde{T} = 0.051167$	
$10^2\tilde{P}$	theory	Tait (modified)	theory	Tait (modified)
2.675	3.85	3.83	8.32	8.26
5.349	3.48	3.48	7.04	7.06
10.698	2.93	2.93	5.39	5.46
16.047	2.54	2.54	4.37	4.44
21.396	2.24	2.23	3.67	3.72
26.745	2.00	2.00	3.17	3.19
32.094	1.81	1.80	2.79	2.78

[a] Theoretical, eq 14; Tait, eq 15, 11′, 12′.

compensation of the variations in C and B seen above. The next step then is to evaluate the respective isothermal compressibilities β, where

$$\tilde{\beta} = -(1/\tilde{V})(\partial\tilde{V}/\partial\tilde{P})_{\tilde{T}} \qquad (13)$$

Substitution of eq A1, A4, and A5 yields

$$\tilde{\beta} = (\tilde{V}/\tilde{T})[\tilde{P}\tilde{V}/\tilde{T} + R/3 + (4y/\tilde{T})(2A\Phi - B)\Phi - X^2/Z]^{-1} \qquad (14)$$

On the other hand, for specified values of C and B we have

$$\tilde{\beta} = C[\tilde{V}(0,\tilde{T})/\tilde{V}(\tilde{P},\tilde{T})]/(\tilde{P} + \tilde{B}) \qquad (15)$$

In Figure 4 the solid lines indicate $\tilde{\beta}$ as a function of $\tilde{P}$ for two temperatures, showing the significant decrease of $\tilde{\beta}$ or increase of the bulk modulus with increasing pressure. A comparison with the predictions of the conventional Tait equation can be made for specific polymers. Here, however, we examine the adequacy of the modified Tait equation, which employs eq 11′ and 12′. The results are displayed in Table I. One concludes that the revised Tait equation provides compressibilities consistent with the theoretical expression. We have tested various simplifications to revert to the original form of this equation; see Figure 4. If, for example, the conventional value of C = 0.0894 and an average for $\tilde{B}$ over the pressure range displayed in Figure 2 are adopted, a maximum deviation of 11% results at the higher $\tilde{T}$ shown. Similar discrepancies ensure by allowing C to vary in accord with eq 11′. Thus it is particularly at elevated temperatures that the change in eq 8 must be introduced.

Discussion

The principal results are eq 6 and 14, to be combined with the equation of state, i.e., the coupled eq 1 and 2. The form of these equations makes the introduction of numerical expressions for practical computations desirable. An improvement over the earlier equation for $\tilde{\alpha}$ at atmospheric pressure reduces the previous dependence on temperature.

The Tait equation, fitted to PVT measurements, has been the convenient way not only for comparisons with theory at elevated pressures but also to derive compressibilities and bulk moduli. A theoretical interpretation rests on eq 10. The present evaluation of this equation indicates significant departures from the constancy of C and the pressure independence of the B function, which are the essence of the Tait equation, even if the universality of the C value is relaxed. Thus eq 8 must be viewed as an empirical relation, useful for a summary description of PVT data in combination with volume–temperature data at atmospheric pressure. However, subsequent conclusions regarding bulk moduli, supposed to be consistent with theory, must be accepted with caution. Instead, eq 11′ and 12′, substituted in eq 15, should be employed for computations consistent with eq 1 and 2.

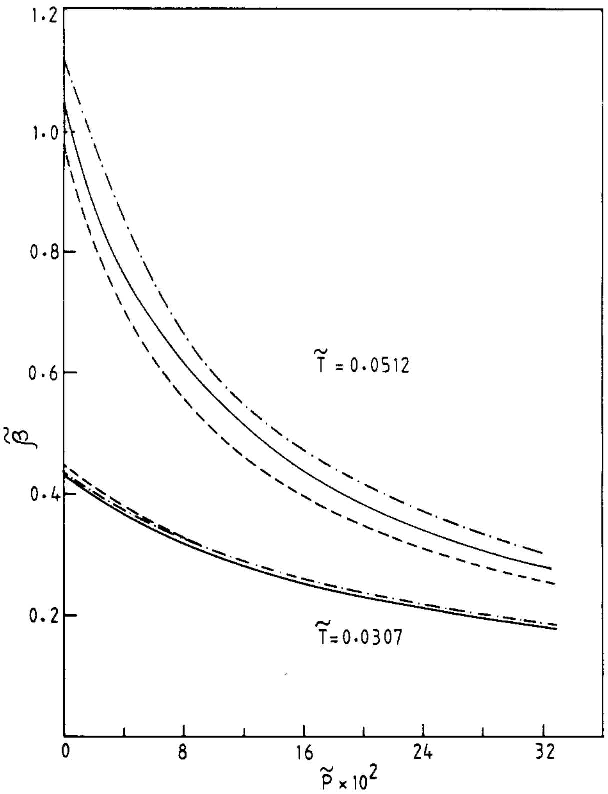

Figure 4. Scaled compressibility $\tilde{\beta}$ vs $\tilde{P}$: (—) eq 14; (- - -) C = 0.0894 and $\tilde{B}$ (average); (- · -) C from eq 11′ and $\tilde{B}$ (average). Average of $\tilde{B}$ is taken over the $\tilde{P}$ range in Figure 2.

The numerical computations and graphs imply a value of $3c/s$ equal to unity, although the analytical expressions are general. The equations of state of mixtures have the identical scaled form as eq 1 and 2, and the dependence on composition appears only in the scaling and other parameters.[10] Therefore, the ratio s/c, which is involved not only in eq 2 for the equilibrium hole fraction $1 - y$ but moreover in the definitions of Z, eq 7, and G following eq 12, varies with composition. This then requires revisions of the numerical approximations presented here for single constituents of high molar mass. Analogous modifications apply to oligomeric compounds due to different numerical values of s/c.[23]

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Appendix

Derivatives required in the text have been developed in ref 5 and 8. Below we cite the pertinent expressions. The equations are presented here in terms of actual rather than scaled variables of state. They are employed in the body of the text in scaled form.

$$(\partial P/\partial V)_T = (\partial P/\partial V)_{T,y} + (\partial P/\partial y)_{T,V}\,(\partial y/\partial V)_T \qquad (A1)$$

$$(\partial^2 P/\partial V^2)_T = (\partial^2 P/\partial V^2)_{T,y} + 2(\partial^2 P/\partial V\partial y)_T\,(\partial y/\partial V)_T + (\partial^2 P/\partial y^2)_{T,V}\,[(\partial y/\partial V)_T]^2 + (\partial P/\partial y)_{T,V}\,(\partial^2 y/\partial V^2)_T \qquad (A2)$$

From eq A1 and A2 there follows

$$(\partial P/\partial V)_{T,y} = -(T/V^2)[PV/T + R/3 + (4y/T)(2A\Phi - B)\Phi] \qquad (A3)$$

where $R = Q(1 - Q)^{-2}$

$$(\partial P/\partial y)_{T,V} = T(yV)^{-1}[\tfrac{2}{3}R - (2y/T)(3A\Phi - B)\Phi] \qquad \text{(A4)}$$

$$(\partial y/\partial V)_T = \{(y/V)[\tfrac{2}{3}R - (2y/T)(3A\Phi - B)\Phi]\}/\{\tfrac{4}{3}R + (y/2T)(9A\Phi - 2B)\Phi + (s/c)[y^{-1}\ln(1-y) + (1-y)^{-1}]\} \qquad \text{(A5)}$$

Differentiation of (A3), (A4), and (A5) gives

$$(\partial^2 P/\partial V^2)_{T,y} = (T/V^3)[PV/T + (R/9)(7 - 5Q) \times (1 - Q)^{-1} + (2y/T)(24A\Phi - 8B)\Phi - (V^2/T)(\partial P/\partial V)_{Ty}] \qquad \text{(A6)}$$

$$(\partial^2 P/\partial V\partial y)_T = [T/(yV^2)][(2y/T)(12A\Phi - 2B)\Phi - \tfrac{2}{9}R(1 + Q)(1 - Q)^{-1} - (yV/T)(\partial P/\partial y)_{V,T}] \qquad \text{(A7)}$$

$$(\partial^2 P/\partial y^2)_{T,V} = [T/(y^2V)][(4y/T)(6A\Phi - B)\Phi - \tfrac{2}{9}R(1 - 5Q)(1 - Q)^{-1}] \qquad \text{(A8)}$$

$$(\partial^2 y/\partial V^2)_T\{\tfrac{4}{3}R + (y/2T)(9A\Phi - 2B)\Phi + (s/c)[y^{-1}\ln(1-y) + (1-y)^{-1}]\} = (y/V^2)[(y/2T)(60A\Phi - 12B)\Phi - \tfrac{4}{9}R(2 - Q)(1 - Q)^{-1}] + (1/V)(\partial y/\partial V)_T[(y/2T)(60A\Phi - 4B)\Phi + \tfrac{2}{9}R(7 + Q)(1 - Q)^{-1}] + (1/y)[(\partial y/\partial V)_T]^2\{(y/2T)(27A\Phi - 2B)\Phi - \tfrac{8}{9}R(1 + Q)(1 - Q)^{-1} + (s/c)[y^{-1}\ln(1-y) + (1-2y)(1-y)^{-2}]\} \qquad \text{(A9)}$$

Insertion of the appropriate quantities in (A1) and (A2) and some further simplification yield eq 9, 11, and 12.

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A Study of Single-Arm Relaxation in a Polystyrene Star Polymer by Neutron Spin Echo Spectroscopy

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ABSTRACT: We have studied 12-arm polystyrene star molecules by elastic and quasi-elastic small-angle neutron scattering. Labeling single arms, we accessed the static and dynamic properties of the star constituents and compared the results with those from a fully labeled star. While the collective dynamic response is characterized by a strong minimum in the reduced relaxation rate, this minimum is absent in the single-arm response. Consequently, the minimum originates from interarm interactions in accordance with its previous characterization as a de Gennes type narrowing.

A star polymer is a macromolecule consisting of many (⩾3) linear homopolymers of nearly identical molecular weight, chemically linked to a common seed molecule which extends no more than a few bond lengths. The presence of the star center implies a strong stretching of the chains due to the crowding of arms near the center region and the subsequent relaxation toward the rims. Thus a star polymer may in a single structure contain monomer concentrations ranging all the way from that of the melt to that of a dilute solution. Even though the behavior of the linear polymers has been successfully described by the scaling theories in general terms, much less is known concerning the properties of a star polymer of finite size. Recently, it has been possible to synthesize monodispersed model star polymers by anionic polymerization. There has been an intense effort in the study of this new class of well-characterized polymers. These efforts include the long-standing theoretical investigations,[1,2] as well as experimental studies by static and dynamic light scattering,[3] small-angle neutron scattering,[4,5] quasi-elastic

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