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Universal Response of Polymers, Solvents, and Solutions to Pressure

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ABSTRACT: It is demonstrated that the compression response of polymers, solvents, and polymer solutions to hydrostatic pressure satisfies a corresponding states principle. A dimensionless pressure variable is used to superpose compression data as a function of temperature into a universal curve. A rigorous thermodynamic analysis is developed to relate isothermal compression to the free energy. The curvature of the free energy as a function of density, in particular its anharmonicity around its minimum, governs the compression response. The apparent independence of the energy curvature to temperature, and in some cases composition, is responsible for the observed universality. The compression response is also relatively insensitive to chemical structure for many polymers. The observed temperature–pressure superposition requires that the free energy satisfy a universal functional form that is derived. Using Padé analysis, a new isothermal equation of state has been obtained. A theoretical bound is placed on the amount of isotropic tension (negative pressure) that a liquid or solid can sustain.

Introduction

Since the early theoretical and experimental work of Simha and co-workers,[1–4] it has been known that polymer *PVT* data satisfy a corresponding states principle. Other theoretical equation of state models have also suggested corresponding states behavior.[5–16] All models predict that density is a function of a dimensionless temperature, $\tilde{T} = T/T^*$, and pressure, $\tilde{P} = P/P^*$. The scale parameters T^* and P^* are constants for a given polymer. These parameters are different for each model and have been recently tabulated for a large number of polymers for several different models.[17,18] Our statement of the corresponding states behavior or universality differs from the above theoretical models; a single dimensionless pressure variable, independent of any model, is used to describe the compression of a liquid or solid. This variable is $(P - P_0)/B_0$ where B_0 is the isothermal bulk modulus evaluated at some convenient reference pressure P_0. It arises in a natural way from a thermodynamic analysis of compression.

The compressional strain ϵ is defined as

$$\varepsilon \equiv \int_{V_0}^{V} \frac{\mathrm{d}V'}{V'} = \ln(V/V_0) = \int_{P_0}^{P} \frac{\partial \ln V}{\partial P}\, \mathrm{d}P \equiv -\int_{P_0}^{P} B^{-1}\, \mathrm{d}P \tag{1a}$$

$$= \int_{P_0}^{P} \frac{\mathrm{d}P}{B_0 + B_1(P-P_0) + \frac{1}{2} B_2(P-P_0)^2 + \ldots}$$

$$= -\Delta p + \frac{1}{2!} B_1(\Delta p)^2 - \frac{1}{3!}(2B_1{}^2 - B_0B_2)(\Delta p)^3 + \ldots \tag{1b}$$

where V is the volume at pressure P, V_0 is the volume at the reference pressure P_0, B is a bulk modulus, and Δp is a dimensionless pressure variable

$$\Delta p \equiv (P - P_0)/B_0 \tag{2}$$

where B_0 is the bulk modulus evaluated at the reference pressure P_0. This dimensionless pressure variable plays a key role in all that follows.

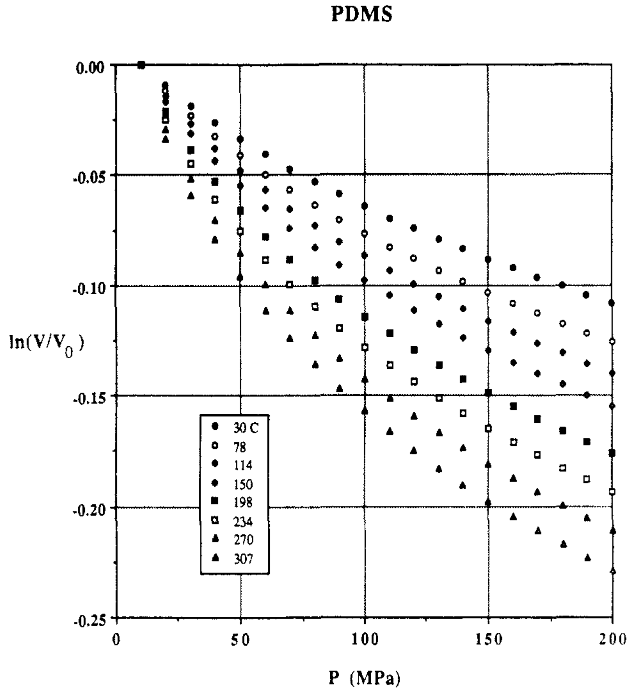

Figure 1. Isothermal compression data[19] for a poly(dimethylsiloxane) (M_w = 1.9 × 10^5) at the temperatures indicated. The reference volume V_0 at each temperature was determined at a reference pressure P_0 of 10 MPa. Note that all isotherms go to zero at 10 MPa. These data are replotted in Figures 2 and 3.

T–P and *T–P–C* Superposition

A typical example of the isothermal compression behavior of a polymer at several temperatures is shown in Figure 1. Note that these data for poly(dimethylsiloxane) (PDMS) cover a wide temperature range (nearly 300 °C).[19] The same data shown in Figure 1 are plotted in Figure 2 as a function of the dimensionless pressure Δp defined in eq 2 using a reference pressure of 10 MPa (100 bar). Note that all data fall onto a single nonlinear curve. This result illustrates temperature–pressure (*T–P*) superposition and implies that compression is a function of Δp only. In turn this requires that the first few coefficients in the expansion for the compressive strain (eq 1b) be *temperature independent*; all of the temperature dependence has been absorbed in B_0. In Table I the experimental values of B_0

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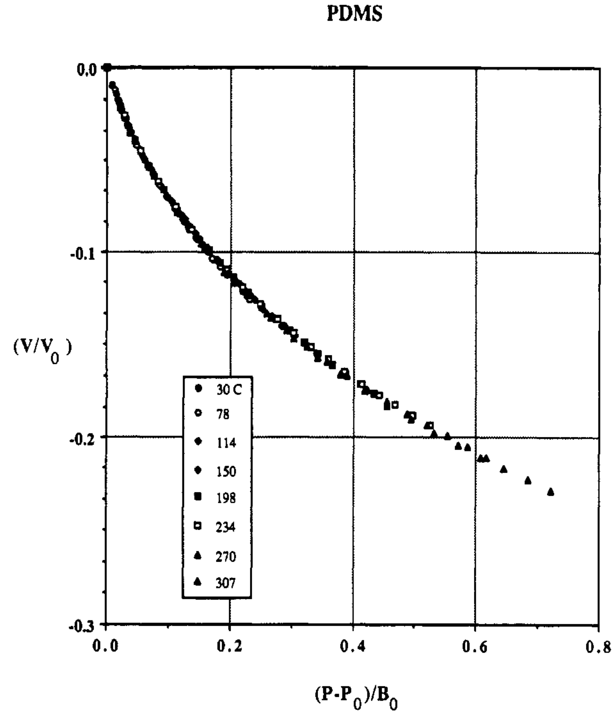

Figure 2. Compression data in Figure 1 replotted against the reduced pressure variable $(P - P_0)/B_0$ where P_0 = 10 MPa and B_0 is the isothermal bulk modulus at 10 MPa for each isotherm. The requisite moduli are tabulated in Table I.

Table I. Isothermal Bulk Moduli (in GPa) for PDMS at the Indicated Temperatures and Pressures

	temp, °C							
P_0 (MPa)	30	78	114	150	198	234	270	307
10	1.04	0.82	0.67	0.56	0.44	0.36	0.31	0.26
140	2.14	1.93	1.87	1.74	1.58	1.47	1.36	1.29

Table II. Isothermal Bulk Moduli (in GPa) at Zero Pressure for Polystyrene/Toluene Solutions at the Indicated Temperatures and Compositions

	temp, °C		
% PS	30	50	80
0	1.0	0.88	0.72
8.2	1.1	0.92	0.75
25.4	1.2	1.1	0.90

are tabulated for PDMS at several reference pressures.

In Figure 3 we have superposed the PDMS data in Figure 1 using reference pressures of 10 and 140 MPa. As can be seen both sets of data beautifully overlap. This result indicates that $\epsilon(\Delta p) = \epsilon(\Delta p')$, if $\Delta p = \Delta p'$. The reference pressure P_0 that is chosen to reduce the data would appear to be unimportant. From a practical viewpoint, more accurate values of B_0 can be obtained at moderate reference pressures than at zero pressure. However, the good agreement seen here for PDMS may be fortuitous (see the Discussion section).

Figure 4 illustrates that the bulk modulus for PDMS also satisfies T–P superposition. This is not a surprise. If compression satisfies T–P superposition, then through eq 1a, the bulk modulus must also satisfy T–P superposition.

In Figure 5 isothermal compression data for toluene solutions of polystyrene as a function of temperature and composition are shown. In Figure 6 the same data are plotted as a function of Δp using zero pressure moduli that illustrates temperature–pressure–composition superposition. Both the temperature and compositional dependence of the compression is taken into account in B_0.

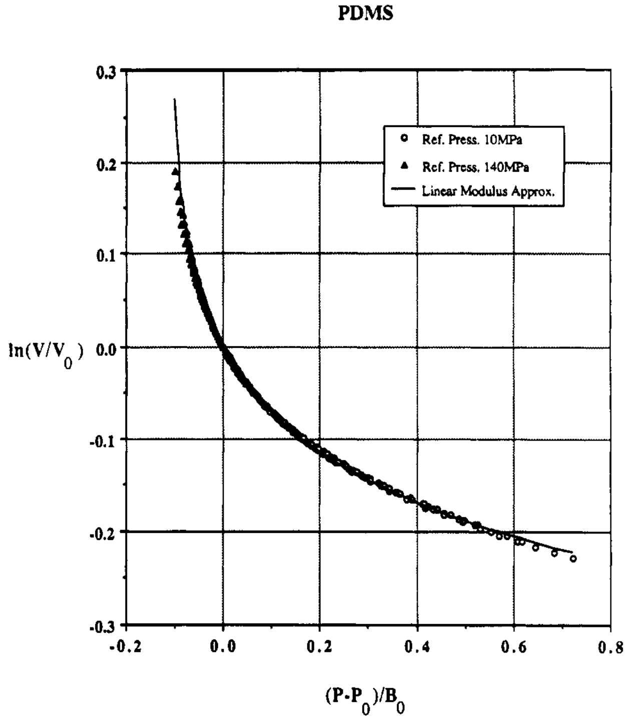

Figure 3. Compression data in Figure 1 replotted using two different reference pressures (10 and 140 MPa). The solid line was calculated using the linear modulus approximation (eq 18b) with B_1 = 9.0. Using a large reference pressure extends data to negative pressures (see text). Moduli are tabulated in Table I.

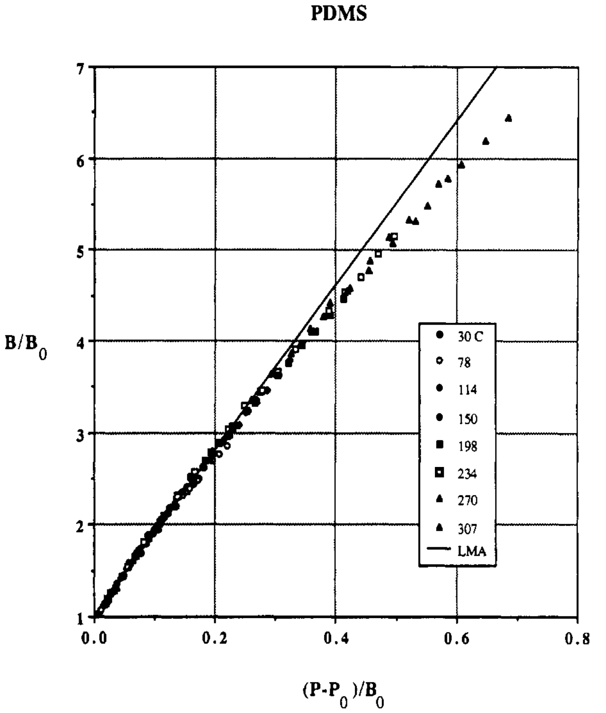

Figure 4. Reduced isothermal modulus for PDMS against reduced pressure using a reference pressure of 10 MPa. The figure illustrates that the modulus satisfies T–P superposition. The straight line shown has a slope of 9.

In Table II the experimental values of B_0 are tabulated for the polystyrene solutions. In Figure 7 compression data for chloroform (CCl_3H) are shown over a large temperature range that illustrates T–P superposition. Note that the highest temperature of 210 °C is nearly 150 °C above the normal boiling point and 53 °C below the critical temperature. These data in Figures 5–7 were obtained on a Gnomix PVT apparatus that has been described in detail

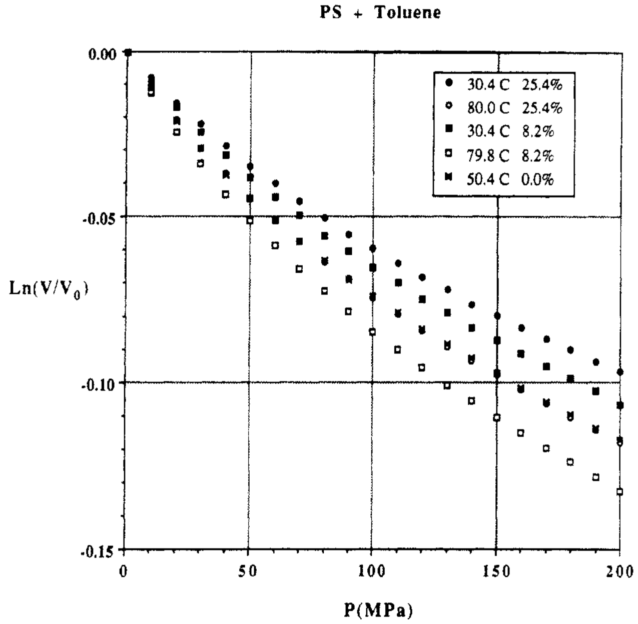

Figure 5. Isothermal compression data for toluene and solutions of toluene and polystyrene ($M_w = 1.06 \times 10^6$) at the indicated temperatures and compositions. The reference volumes V_0 were determined at atmospheric pressure ($P_0 = 0$). These data are replotted in Figure 6.

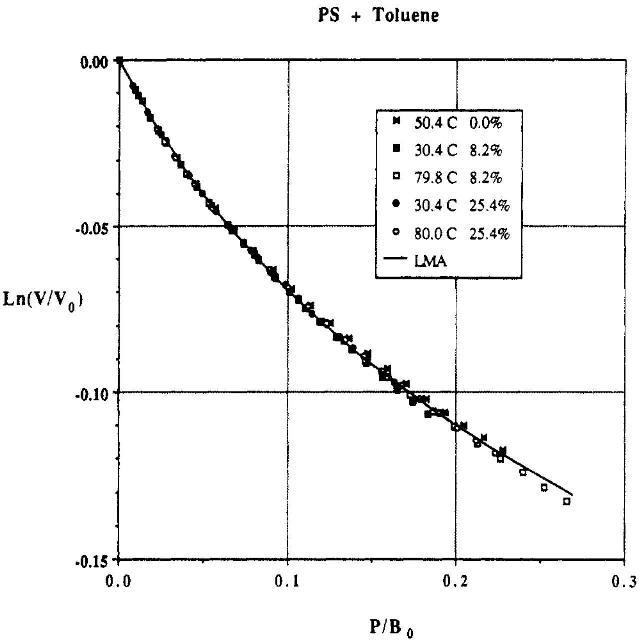

Figure 6. Example of T–P–C superposition. Solution data in Figure 5 are plotted against reduced pressure using a zero reference pressure. Moduli used to construct the plot are tabulated in Table II. The solid line was calculated using the linear modulus approximation (eq 18b) with $B_1 = 10$.

elsewhere.[20] Moduli for chloroform are tabulated in Table III.

General Thermodynamic Analysis

A preliminary account of this analysis for $P_0 = 0$ under adiabatic conditions has already been given.[21] What follows below is an account for isothermal compression with respect to an arbitrary reference pressure P_0.

The isothermal response of a liquid or solid to pressure is directly related to the Helmholtz free energy A by the thermodynamic relation

$$-P = \left.\frac{\partial A}{\partial V}\right)_T \tag{3}$$

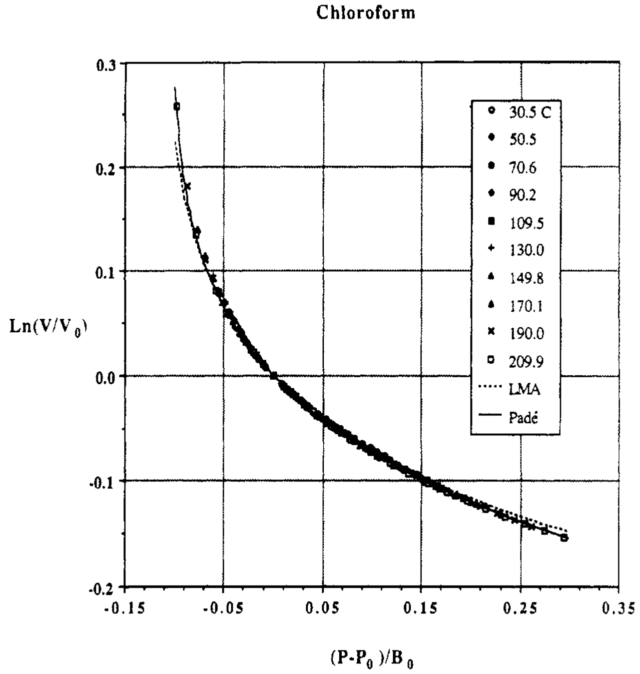

Figure 7. Compression T–P superposition for chloroform (CCl_3H) over a large temperature range. The reference pressure is 50 MPa. Moduli used to construct the plot are tabulated in Table III. The dashed line was calculated using the linear modulus approximation (eq 18b) with $B_1 = 8.5$. The solid line was calculated using the Padé approximation (eq 39a) with $B_1 = 8.3$ and $\omega = 0.85$.

Table III. Isothermal Bulk Moduli (in GPa) at 50 MPa at the Indicated Temperatures for Chloroform

temp, °C									
30.5	50.5	70.6	90.2	109.5	130	149.8	170.1	190	209.0
1.33	1.25	1.11	1.02	0.90	0.81	0.73	0.65	0.57	0.51

It is convenient to define a dimensionless relative density ρ

$$\rho = V_0/V \tag{4}$$

where V_0 is the volume at temperature T and pressure P_0. Thus, from eq 3

$$P = -\left.\frac{\partial A}{\partial \rho}\right)_T \left.\frac{\partial \rho}{\partial V}\right)_T = \frac{\rho^2}{V_0}A'(\rho,T,P_0) \tag{5}$$

where the prime on A indicates a derivative with respect to ρ. The general behavior of A is illustrated in Figure 8.

The isothermal bulk modulus B is defined by

$$B \equiv -V\left.\frac{\partial P}{\partial V}\right)_T = \frac{\rho^2}{V_0}[\rho A''(\rho,T,P_0) + 2A'(\rho,T,P_0)] \tag{6}$$

At the reference pressure P_0

$$B_0 = [A_2 + 2A_1]/V_0 \equiv A_{21}/V_0 \tag{7}$$

where

$$A_1 = A'(1,T,P_0), \quad A_2 = A''(1,T,P_0) \tag{8}$$

Thus, eq 5 can be rewritten as

$$(P - P_0)/B_0 \equiv \Delta p = (\rho^2 A' - A_1)/A_{21} = (\rho^2 A' - P_0V_0)/B_0V_0 \tag{9}$$

This is the isothermal equation of state. Note that Δp only depends on the curvature of the free energy, i.e., its second derivative, $A''(\rho,T,P_0)$. The value of A_1 is an arbitrary constant defined by the arbitrary reference pressure P_0. Expansion of the right-hand side of eq 9 around $\rho = 1$ is completely determined by A_2 and higher order derivatives. In general, the right-hand side of eq 9

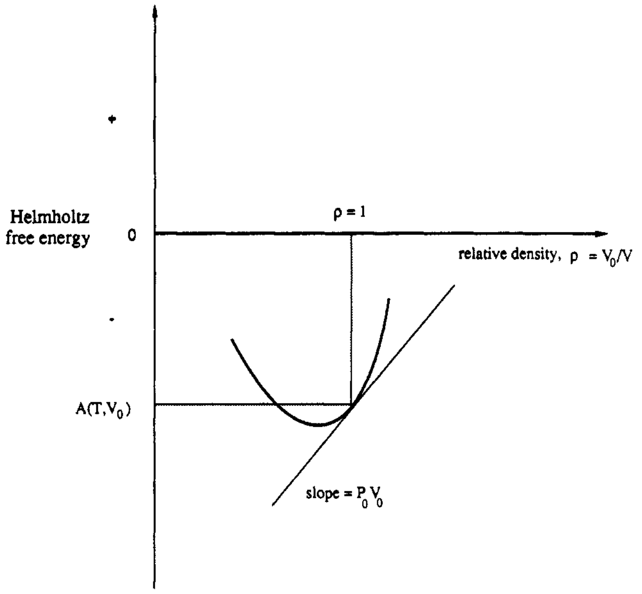

Figure 8. Schematic of how the Helmholtz free energy varies with relative density, (V_0/V), for a liquid or solid. In contrast, the free energy of an ideal gas is monotonic in density. The balance between attractive and repulsive interactions in condensed matter gives rise to the minimum.

is a function of ρ and T. If it was a function of ρ only, then the isothermal compressive strain, $\epsilon = -\ln \rho$, would be a function of Δp only. For a given material, all isothermal compressions would follow the same universal curve determined by the inverse of $(\rho^2 A' - A_1)/A_{21}$.

We can carry out the requisite inversion by first expanding the right-hand side of eq 9 in a series around $\rho = 1$ and then inverting the series:

$$\rho = 1 + \Delta p - \frac{1}{2!}\left(4 + \frac{A_{31}}{A_{21}}\right)\Delta p^2 + \frac{1}{3!}\left[42 + 18\left(\frac{A_{31}}{A_{21}}\right) + 3\left(\frac{A_{31}}{A_{21}}\right)^2 - \frac{A_{41}}{A_{21}}\right]\Delta p^3 - ... \quad (10)$$

where

$$A_{n1} = A_n + (-1)^n n! A_1 \quad (11)$$

The negative logarithm of ρ yields a series expansion for ϵ:

$$\epsilon = \sum_{n=1}^{\infty} \frac{c_n}{n!} \Delta p^n \quad (12)$$

with the first few coefficients given by

$$c_1 = -1$$

$$c_2 = 5 + A_{31}/A_{21}$$

$$c_3 = -[56 + 21(A_{31}/A_{21}) + 3(A_{31}/A_{21})^2 - A_{41}/A_{21}] \quad (13)$$

Note that the c_n are dimensionless parameters that in general depend on temperature and P_0.

A somewhat more direct route to eq 13 is to evaluate the pressure derivatives of the bulk modulus at $\rho = 1$ by using eq 7 and the relation $\partial B/\partial P)_T = \partial \ln B/\partial \ln \rho)_T$. This yields

$$B/B_0 = B_0^{-1} \sum_{n=0}^{\infty} \frac{B_n}{n!}(P - P_0)^n = B_0^{-1} \sum_{n=0}^{\infty} \frac{B_0^{\,n} B_n}{n!} \Delta p^n \quad (14)$$

with

$$B_1 = 5 + A_{31}/A_{21}$$

$$B_0 B_2 = -[6 + A_{31}/A_{21} + (A_{31}/A_{21})^2 - A_{41}/A_{21}] \quad (15)$$

Substitution of these results into eq 1b yields eqs 12 and 13 as it should.

Taking the isothermal pressure derivative of the bulk modulus yields the following differential equation for the Helmholtz energy:

$$\rho^2 A''' + \rho[5 - (\partial B/\partial P)]A'' + [4 - 2(\partial B/\partial P)]A' = 0 \quad (16)$$

This equation is exact and it can be solved in various approximations; the simplest is to assume that the modulus varies linearly with pressure so that $(\partial B/\partial P) = B_1$. Under this approximation and the boundary conditions $A_1 = P_0 V_0$ and $A_{12} = B_0 V_0$, we obtain

$$A'(\rho,T,P_0) = \frac{B_0 V_0(\rho^{B_1} - 1) + P_0 V_0 B_1}{B_1 \rho^2} \quad (17)$$

or, by using the equation of state (eq 9), we obtain

$$(P - P_0)/B_0 \equiv \Delta p = (\rho^{B_1} - 1)/B_1 \quad (18a)$$

which can also be written as

$$\epsilon = -\ln(1 + B_1 \Delta p)/B_1 \quad (18b)$$

Equation 18b has the functional form of the Murnaghan equation.[23,24] Note that it can also be derived directly from eq 1a under the linear approximation $B \cong B_0 + B_1(P - P_0)$.[22] We will call this the *linear modulus approximation.*

Implications of *T*–*P* Superposition

Temperature–pressure superposition requires that the Helmholtz free energy satisfy a universal functional form that we can deduce from the equation of state (eq 9):

$$(\rho^2 A' - P_0 V_0)/B_0 V_0 = \Delta p = F(\rho) \quad (19)$$

where $F(\rho)$ is a function of ρ only. Equation 19 follows because the compression ϵ, or equivalently ρ, satisfies T–P superposition; i.e.

$$\rho = F^{-1}(\Delta p) \quad \text{and} \quad \epsilon = -\ln F^{-1} \quad (20)$$

where F^{-1} is the inverse of F. Integrating eq 19, we obtain

$$A - A_0 = B_0 V_0 f(\rho) + P_0 V_0(1 - 1/\rho) = B_0 V_0 f(\rho) + P_0(V_0 - V) \quad (21)$$

where f is a dimensionless free energy function:

$$f(\rho) = \int_1^{\rho} [F(\rho)/\rho^2]\, d\rho \quad (22a)$$

and note that

$$f'(\rho) = F/\rho^2 = \Delta p/\rho^2 \quad (22b)$$

It can be easily verified from eq 21 that

$$f(1) \equiv f_0 = 0; \quad f'(1) \equiv f_1 = 0; \quad f''(1) \equiv f_2 = 1 \quad (23)$$

i.e., f has a minimum at $\rho = 1$. Also from eq 21 it is easy to show that

$$A_{n1} = B_0 V_0 \frac{\partial^n f}{\partial \rho^n}\bigg|_{\rho=1} \equiv B_0 V_0 f_n \quad (24)$$

and thus

$$A_{n1}/A_{21} = f_n/f_2 = f_n \tag{25}$$

Also from eq 6 and the definition of the modulus, we have

$$B/B_0 = \begin{cases} \partial \Delta p/\partial \ln \rho \\ \partial F(\rho)/\partial \ln \rho \\ 1/\partial \ln F^{-1}/\partial \Delta p \end{cases} \tag{26}$$

The isothermal change in the Gibbs free energy or chemical potential μ is also given by several equivalent forms:

$$\mu - \mu_0 = -\int_{V_0}^{V} B \; \mathrm{d}V = B_0 V_0 \int_{1}^{\rho} \partial F/\partial \rho \; \mathrm{d} \ln \rho$$

$$= B_0 V_0 \begin{Bmatrix} f + F/\rho \\ \partial(\rho f)/\partial \rho \\ f + \Delta p/\rho \end{Bmatrix} = B_0 V_0 f + (P - P_0) V \tag{27}$$

The isothermal entropy change is given by

$$S - S_0 = \int_{V_0}^{V} \alpha B \, \mathrm{d}V = -\partial(\mu - \mu_0)/\partial T)_P \tag{28}$$

where α is the thermal expansion coefficient. This yields:

$$S - S_0 = -B_0 V_0 \begin{cases} \dfrac{\alpha_0 \Delta p}{\rho} + f(\alpha_0 + \dfrac{\partial \ln B_0}{\partial T}) \\ \alpha_0 \dfrac{\partial(\rho f)}{\partial \rho} + f \dfrac{\partial \ln B_0}{\partial T} \end{cases} \tag{29}$$

where α_0 is the thermal expansion coefficient at the reference pressure P_0 and we have used $(\partial \rho/\partial T)_P = \rho(\alpha_0 - \alpha)$. Since the internal energy U equals $A + TS$, we also have

$$U - U_0 = B_0 V_0 \left[f\left(1 - \frac{\partial \ln B_0}{\partial \ln T}\right) - T\alpha_0 \frac{\partial(\rho f)}{\partial \rho} \right] + P_0(V_0 - V) \tag{30}$$

Equations 19–30 are quite general for any material that satisfies T–P superposition. These functional forms will provide future guidance to theoretical models that hope to successfully describe T–P superposition. None of the existing theoretical models[3-16] appear to satisfy these functional forms.

In the linear modulus approximation, F and its inverse F^{-1} are given by (*cf.* eq 18):

$$F = (\rho^{B_1} - 1)/B_1 = \Delta p; \quad F^{-1} = (1 + B_1 \Delta p)^{1/B_1} = \rho \tag{31}$$

Thus, eq 26 for the bulk modulus yields the equivalent representations:

$$B = B_0 \rho^{B_1} = B_0(1 + B_1 \Delta p) = B_0(P_0) + B_1(P - P_0) = B_0(0) + B_1 P \tag{32}$$

The dimensionless free energy function $f(\rho)$ is obtained from eq 22a:

$$f(\rho) = \frac{1}{B_1}\left[\frac{\rho^{B_1 - 1} - B_1}{B_1 - 1} + \frac{1}{\rho}\right] \tag{33}$$

These are specific results for F, F^{-1}, and f in the linear modulus approximation.

Padé Approximation

As can be seen from Figure 4, the modulus for PDMS is not linear over the entire pressure range and it has slight negative curvature. Similar small negative curvatures at high pressures have also been seen in normal pentanes and isopentanes[28] and in water.[21] The negative curvature in the modulus suggests that adding a negative quadratic term to the modulus ($B_2 < 0$) would improve things. It does, but, technically, this is not a very satisfactory solution to the problem. A modulus is obtained that eventually goes to zero at a finite pressure.[24] This is a nonphysical result. It implies that the compressed volume approaches zero at a large, but finite, pressure. The well-known Tait equation suffers from the same technical defect.[24] The situation can in principle be remedied by adding a positive cubic term ($B_3 > 0$). This causes the modulus to diverge as P^3 with positive curvature at high pressures, a property without experimental support. Any finite polynomial used to represent the modulus will have difficulty in the large pressure limit. However, if the negative curvature in the modulus persists to very high pressures, a property that seems physically very reasonable, then the modulus would diverge as P^ω where ω *is a positive constant less than 1.*[29] Stated mathematically, we have

$$\lim_{P \to \infty} \frac{\partial \ln B}{\partial \ln P} = \omega \tag{34}$$

We can estimate ω by using a Padé analysis. The procedure is as follows: From the Taylor series expansion in pressure for B (see eq 14), the series for $\ln B$ is obtained. The derivative with respect to pressure is then taken to obtain a Taylor series for $\partial \ln B/\partial \ln \Delta p$. From this series a diagonal Padé approximate $[n, n]$ is formed. For the simplest $[1, 1]$ approximate, we obtain

$$\frac{\partial \ln B}{\partial \ln \Delta p} = \frac{B_1 \Delta p}{1 + (B_1 - B_0 B_2/B_1)\Delta p} \equiv \frac{B_1 \Delta p}{1 + B_1 \Delta p/\omega} \tag{35}$$

As pressure or Δp goes to infinity, we see that the Padé approximate predicts that

$$\omega = B_1^{\,2}/(B_1^{\,2} - B_0 B_2) \tag{36}$$

The experimentally observed negative curvature implies that $B_2 < 0$ and thus ω will be less than unity as required.

Integrating eq 35 yields

$$B = B_0(1 + B_1 \Delta p/\omega)^\omega \tag{37}$$

Notice that, if $B_2 = 0$, then $\omega = 1$ and we recover the linear modulus approximation. Also the Padé approximation for B upon expansion yields the correct first- and second-order coefficients and approximations for all higher order coefficients $B_0{}^{n-1}B_n$:

$$B = B_0\left[1 + B_1 \Delta p + \frac{1}{2} B_0 B_2 \Delta p^2 + \frac{1}{3!}\frac{(2 - \omega)(1 - \omega)}{\omega^2} B_1^{\,3} \Delta p^3 + \ldots\right] \tag{38}$$

where from eq 36, $B_0 B_2 = -B_1{}^2(1 - \omega)/\omega$.

Substitution of eq 37 into eq 1a and integration yields the following for the compression, ϵ ($\omega \neq 1$):

$$\epsilon = \frac{\omega}{(1 - \omega)B_1}[1 - (1 + B_1 \Delta p/\omega)^{1-\omega}] = -\ln F^{-1} \tag{39a}$$

In the special case of $\omega = 1$, eq 18b is obtained instead. Inverting eq 39a yields

$$\Delta p = \frac{\omega}{B_1}\left[\left(1 + \frac{1 - \omega}{\omega} B_1 \ln \rho\right)^{1/(1-\omega)} - 1\right] = F \tag{39b}$$

so that, from eq 26 or eq 37, the modulus has the alternative density representation:

$$B/B_0 = \left[1 + \frac{1-\omega}{\omega}B_1 \ln \rho\right]^{\omega/(1-\omega)} \qquad (40)$$

Although we were unable to obtain a closed-form analytical expression for the free energy function, $f(\rho)$, its density expansion is

$$f(\rho) = \frac{1}{2}(\rho - 1)^2 + \frac{1}{3!}(B_1 - 5)(\rho - 1)^3 + \frac{1}{4!}\left[26 - 9B_1 + \frac{(2\omega - 1)}{\omega}B_1^{\,2}\right](\rho - 1)^4 + \ldots \qquad (41)$$

The Padé approximation will always fit compression data a little bit better than the linear approximation (2 adjustable parameters versus 1). However, for PDMS, the statistical improvement is minimal; using $B_1 = 9.0$, the linear approximation fits the PDMS compression data shown in Figure 3 satisfactorily. For the chloroform data shown in Figure 7, the Padé approximation does visibly better. The Padé approximation may prove useful in extrapolating low-pressure data to higher pressures.

Discussion

The equations developed here are applicable to liquids and isotropic solids. The only assumption made is that the Helmholtz energy is analytic near its minimum. However, the materials should be homogenous and undergo no phase change during compression. For glasses, we assume that the glass is in quasi-equilibrium. This condition prevails at temperatures below the glass transition region. *PVT* measurements in the glass transition region do not satisfy the requirement of quasi-equilibrium. Previously, we showed that both glass and liquid polystyrene compression data could be superposed.[21]

We have shown that isothermal compression data measured over a range of temperatures can be superposed into a single universal curve that is only a function of $(P - P_0)/B_0 \equiv \Delta p$. This is only possible if the first few coefficients in eq 1b or eq 12 are temperature independent. The modulus coefficients $B_0^{\,n-1}B_n$ and the compression coefficients c_n are functions of the derivative ratios A_{n1}/A_{21} as shown in eqs 13 and 15. From eq 25, *T–P* superposition requires that these derivative ratios equal constants. The first few inverse relationships are

$$A_{31}/A_{21} = B_1 - 5 = c_2 - 5 = f_3 \qquad (42)$$

$$A_{41}/A_{21} = 26 - 9B_1 + B_1^{\,2} + B_0B_2 = 26 - 9c_2 + 3c_2^{\,2} + c_3 = f_4 \qquad (43)$$

These temperature-independent derivative ratios define the curvature of the dimensionless free energy function $f(\rho)$. *The experimentally observed T–P superposition indicates that the curvature of the free energy is temperature invariant.*

How far do we expect *T–P* superposition to work with respect to the choice of the reference pressure, P_0? Should all compression curves superpose for arbitrary choice of P_0? In Figure 3 we have shown that *T–P* superposition obtains for PDMS at $P_0 = 10$ and 140 MPa. We can only show that, if the reduced modulus varies linearly with pressure, *T–P* superposition should be independent of the choice of P_0. However, at 140 MPa, the modulus of PDMS is already showing negative curvature (see Figure 4) and it is surprising that such good superposition has been obtained. It may or may not be fortuitous. This question needs more investigation.

Attractive interactions are necessary for the existence of condensed matter and the qualitative behavior in the free energy illustrated in Figure 8. Rewriting eq 42, we have

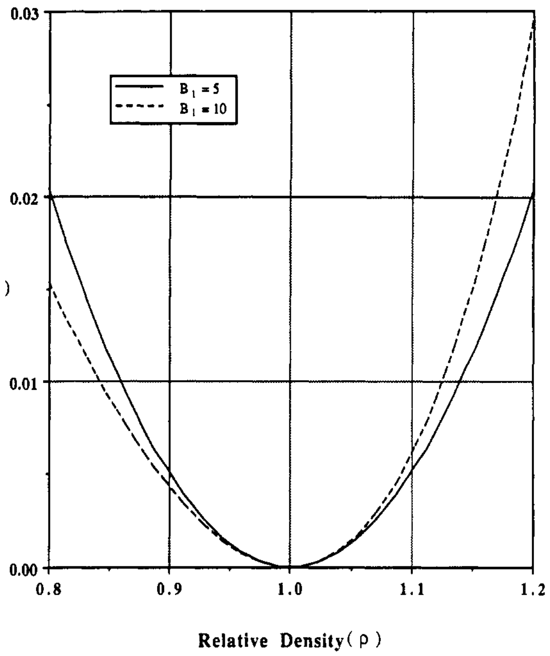

Figure 9. Plot of the dimensionless free energy f against relative density in the linear modulus approximation (eq 33). Note that for $B_1 = 5$ the free energy is very symmetric around its minimum. Most polymers have B_1 values between 9 and 13. The Helmholtz and Gibbs free energies are related to f by eqs 21 and 27.

$$B_1 = 5 + A_{31}/A_{21} = 5 + f_3 \qquad (44)$$

f_3 is a measure of the asymmetry or anharmonicity of the free energy minimum. If $f_3 = 0$, the potential f is quadratic to first order, i.e., a harmonic potential. This means that compression and dilation relative to the reference pressure P_0 are equally difficult. A positive f_3 indicates that compression is more difficult than dilation. Intuitively, we would expect the latter situation to prevail so that $B_1 > 5$. However, in strongly interacting materials, such as ionic salts and liquid metals, $B_1 \approx 5$.[21]

In the linear modulus approximation, the potential f is given by eq 33. Expansion of f in a series yields

$$f(\rho) = \frac{1}{2}(\rho - 1)^2 + \frac{1}{3!}(B_1 - 5)(\rho - 1)^3 + \frac{1}{4!}(B_1^{\,2} - 9B_1 + 26)(\rho - 1)^4 + \ldots] \qquad (45)$$

This functional form of the free energy should be accurate for small displacements around $\rho = 1$ because the approximation that the bulk modulus varies linearly with pressure should hold. In Figure 9, the dimensionless free energy (eq 33) is plotted for $B_1 = 5$ and 10. As can be seen, the free energy is very symmetric around $\rho = 1$ for $B_1 = 5$; note from eq 45 the third order term is zero for $B_1 = 5$. However, the free energy is very asymmetric in pressure. Equation 18b indicates that $\rho \rightarrow 0$ as $\Delta p \rightarrow -1/B_1$, or equivalently, $P \rightarrow -B_0(0)/B_1$, a negative pressure. In Figure 10 the density is plotted as a function of the reduced pressure. The linear modulus approximation places a bound on the amount of isotropic tensile stress that the material can sustain. (As can be seen from eq 39, allowing for the negative curvature in the modulus reduces this bound by a factor ω.) This is a mechanical limit for isothermal, isotropic dilation or "stretching" of the liquid or solid; it is the stress required to overcome attractive forces. Typically, the low-pressure modulus of a polymer is 1 GPa (10^4 bars) and $B_1 \approx 10$. Thus, the maximum "breaking stress" of a polymer should be about 10^2 MPa.

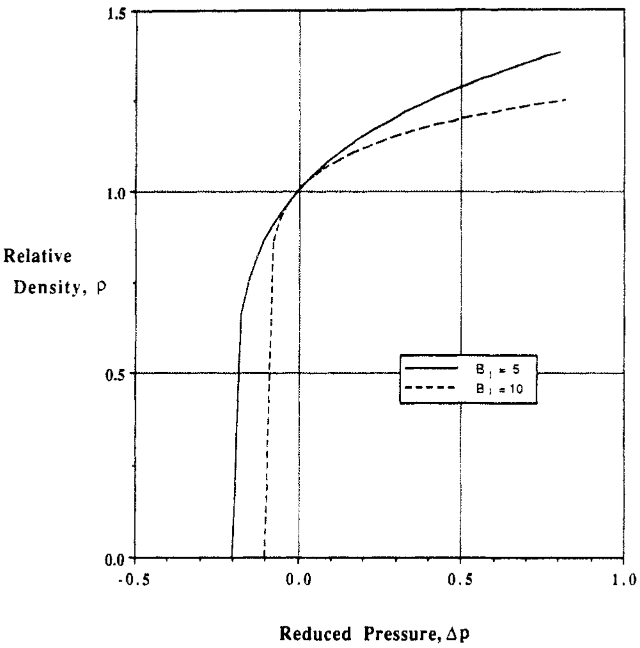

Figure 10. Plot of the relative density against reduced pressure in the linear modulus approximation (eq 31). Note that the density approaches zero at a finite negative reduced pressure of $-1/B_1$. This is a theoretical limit for the maximum negative pressure that condensed matter can support.

But a polymer will fail or "yield" well before this maximum stress is reached. In a liquid, we expect cavitation[26] to occur prior to reaching this limit. To our knowledge, dilatational experiments on polymer liquids have never been reported, although water has been extensively studied at negative pressures.[27]

The temperature–pressure–concentration (T–P–C) superposition illustrated in Figure 6 for toluene solutions of polystyrene obtains because pure polystyrene and toluene have similar compression behavior. Thus, mixtures of these components should have similar compression behavior. The maximum polymer concentration that we have investigated is 25 wt %. At higher polymer concentrations, the solutions are very viscous and removing gas bubbles from these solutions is difficult. This limits the range of compositions that can be easily investigated.

It is remarkable that the compression response of polymers of widely varying chemical structure is so similar. The compression response is largely governed by how fast the modulus rises with pressure as measured initially by B_1. The pressure coefficient of the modulus B_1 for 29 polymers that we have examined is 11.0 ± 1.5. To put this spread in B_1 values in perspective, the experimental uncertainty in B_1 for a given polymer is about ± 1.

The key experimental variable required in developing these universal compression curves is the isothermal bulk modulus B_0. The experimental determination of B_0 at low pressures (or effectively zero pressure) is notoriously difficult to determine accurately; 5–10% errors are common.[25] Typically, the lowest pressure for which compression is measured for polymers is 10 MPa. Less error is involved in determining B_0 at moderate pressures. Our procedure for determining B_0 at a reference pressure P_0 is to fit ln V data in the immediate vicinity of P_0 to a quadratic equation. The reciprocal of the linear coefficient is taken as the modulus for that P_0. The modulus normally decreases exponentially with temperature,[18] so that, if B_0 is determined as a function of temperature, a smoothing of the B_0 data can be achieved. Many investigators fit the Tait equation,[18,24] with a universal value of $C = 0.0894$, over the entire pressure range using $B_0(0)$ as an adjustable parameter. In our opinion, this can yield biased zero pressure values of B_0. Taking $C = 0.0894$ in the Tait equation is equivalent to assuming that $B_1 = 10.2$ for all polymers because for the Tait equation $B_1 = 1/C - 1$. As previously mentioned, we have found $B_1 = 11.0 \pm 1.5$.

Equation 18, based on the approximation that the modulus varies linearly with pressure, is rigorously correct for an ideal gas. For an ideal gas, $B_0 = P_0$, $B_1 = 1$, and all higher pressure derivatives B_n are zero. Substitution of these results into eq 18a yields $PV = P_0V_0$ as it should for isothermal compression or expansion. The analogous adiabatic equation of state[21] yields the correct $PV^{\gamma} = P_0V_0^{\gamma}$ since $B_0 = \gamma P_0$ and $B_1 = \gamma$ where γ is the heat capacity ratio. Also note that $A' \sim 1/\rho$ and $A \sim \ln \rho \sim -\ln V$ as it should for an ideal gas. For an ideal gas, A varies monotonically with density and does not have a minimum.

We conclude this discussion with a speculation. Solid polymers have been extensively studied under uniaxial tension. It is well-known that dilation occurs during uniaxial tension as measured by Poisson's ratio, μ. It is easy to show that the dilation that occurs during uniaxial tension is given by

$$V/V_0 = (L/L_0)^{(1-2\mu)} = 1/\rho \qquad (46)$$

where L_0 is the initial length of the specimen under zero tension and L is the length under uniaxial tension. The polymer yields or "fails" at some finite strain. Yield and tensile strengths for polymers are very comparable and usually fall in the range 10–80 MPa.[30] The yield strain is poorly defined for a glassy polymer, but usually at 10% strain we are beyond the elastic limit, or in some cases, the failure strain. If we arbitrarily define the yield strain as 0.1, i.e., we declare that the material has yielded or "failed" when $(L-L_0)/L_0 = 0.1$; then we can calculate the failure stress using eqs 18a and 46. Using a typical Poisson's ratio of 0.35, we obtain $\rho = 0.97$ and a failure stress of $B_0(1 - 0.97^{10})/B_1 \cong B_0/40 \cong 50$ MPa (typical values of B_0 are 1–3 GPa[30]). This very crude and speculative calculation suggests that failure under uniaxial tension may be closely related to the attendant dilation.

Summary

(1) Polymers and organic solvents (possibly all liquids and isotropic solids?) satisfy T–P superposition; i.e., compression data for a given polymer or solvent over a range of temperatures can be superposed into a universal curve by plotting the data as a function of the dimensionless pressure variable, $\Delta p \equiv (P - P_0)/B_0$.

(2) If polymer and solvent have similar compression behavior, as say measured by the pressure coefficient of the bulk modulus, B_1, then the compression of their solutions should satisfy T–P–C superposition. This has been illustrated for toluene solutions of polystyrene.

(3) Although we have focused on PDMS, we have observed T–P superposition in all polymers (29) and solvents (5) that we have studied. Even water, which has an anomalous modulus that passes through a maximum with temperature, satisfies T–P superposition.[21] The compression behavior of many polymers, widely varying in chemical structure, is very similar. For 29 polymers that we have examined, $B_1 = 11.0 \pm 1.5$.

(4) T–P superposition implies that the free energy satisfies a universal functional form (see eqs 19–30). In particular, the curvature properties of the free energy are temperature independent. This further implies that the reduced pressure derivatives of the modulus, $B_0^{n-1}B_n$ (n

$\geq$ 1), are temperature independent. These universal functional relations will provide future guidance for theoretical model development.

(5) Two approximations have been derived for universal compression. The first assumes the bulk modulus varies linearly with pressure (eq 18). It is a one-parameter equation (B_1). The second approximation assumes that the modulus diverges with pressure as P^{ω} where ω is a positive constant less than unity. A Padé analysis of this behavior yields the isothermal equation of state (eq 39). The Padé approximation involves two parameters, the first and second pressure derivatives of the bulk modulus (B_1 and B_2). The Padé approximation is only necessary for systems that exhibit significant negative curvature in the modulus. For the polymers that we have studied, including PDMS, the linear modulus approximation affords an excellent approximation to compression data. For the chloroform data shown in Figure 7, the Padé approximation does visually better. The Padé approximation may prove useful in extrapolating low-pressure data to higher pressures.

(6) A liquid or solid under isotropic tension (negative pressure) will fail prior to the pressure reaching a negative value of $-B_0/B_1$. This is a bound on the amount of negative pressure a substance can sustain. At a given temperature, B_0/B_1 is a measure of the strength of attractive forces.

(7) It is speculated that the failure of a solid polymer under uniaxial tension may be related to the attendant dilation.

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