Further Refinement of the Self-Consistent Model for the Dependence of Polyethylene Elastic Constants upon Density[1]

Jay Janzen[2]

---

[1]Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado

ABSTRACT

This report refines and extends earlier work having to do with the dependence of elastic constants of polyethylenes upon density alone, irrespective of molecular architectural and crystalline morphological details.

It was argued previously that the coupled set of binary microcomposite mechanical property mixing rules known as the "self-consistent scheme" ("scs") derived by Hill, Budiansky, and Berryman is the only known viable approach to explaining, quantitatively, the stiffness-density relationship observed across a wide density range in semicrystalline polyethylenes.

Upon critical re-examination of the sparse data available in the open literature on bulk moduli and sonic velocities in these materials, however, it has become evident that revision is needed in the aspects of the earlier work that dealt with these properties.

Specifically, much-improved agreement has been found between the scs and measured bulk-modulus values reported by Zoller, by Olabisi and Simha, and by Beret and Prausnitz, among others. This finding leads to clear discernment of disparities between observed sound propagation velocities and predictions of those velocities from elastic constants measured under static or near-static conditions. These disparities are well rationalized in terms of the known strong dependence of the shear modulus of the amorphous component upon deformation rate. (This dependence was ignored in the original development.)

The conclusion is that the self-consistent scheme now appears to be even more strongly supported and generally applicable as an accurate framework for modeling small-deformation mechanical properties of isotropic polyethylenes than was recognized earlier.

KEY WORDS: polyethylene; compressibility; elastic constants; sonic velocity

---

[2]Phillips Petroleum Co. Research Center, Bartlesville, Oklahoma 74004

0. PROLOGUE

"A model should be regarded as suspect if it yields inferences in serious conflict with ANY of the pertinent properties of a system, regardless of how closely it can be made to agree with some, especially if there are adjustable parameters. A model that is consistent with all properties, even if only approximately, can probably be made more precise, but if it is in irreconcilable conflict with any part of the evidence, it is destined to be discarded, and in the meantime, predictions and extrapolations based upon it should be regarded as unreliable."

—Joel H. Hildebrand

"Theories and Facts about Liquids"

Faraday Disc. Chem. Soc. **66** (1978), 151-159

1. INTRODUCTION

In studies of the stiffness-density relationship in unoriented polyethylenes at room temperature carried out in 1989-90 and published in 1992, [1] I argued that the so-called "self consistent scheme" ("scs") formulated by Hill [2] and Budiansky, [3] and subsequently independently rederived by Berryman [4] is the only available binary microcomposite mechanical properties theory that is viable for explaining, quantitatively, the commonly known density dependence of polyethylene stiffness.

Subsequently, Register [5] discovered that removal of interlaboratory contributions to testing variability rendered the agreement between the scs theory for Young's modulus and a large mass of internally consistent experimental evidence to be much better than had been found in the original work, [1] and he also showed very easy extensions to cover two additional small-strain properties commonly compiled, namely yield stresses and strains. These successes have encouraged us to place increasing reliance upon the scs as a valid framework for interpreting small-deformation mechanical property data in polyolefins, and to seek extensions and additional applications.

An especially appealing feature of the self-consistent scheme, which distinguishes it from several other binary mixing rules to be found in the literature for one mechanical property at a time,

is this: because they are built-in, the scs always satisfies the interdependencies[3] amongst elastic constants that are well known [6, 7] in continuum elasticity. Reference 1 paid considerable attention to establishing simultaneous semi-quantitative (at least) agreement between the scs formulation and whatever data could be gathered from the literature on the coupled moduli E (Young's), G (shear), K (bulk or compression), and Λ (Lamé's), along with ν (Poisson's ratio) and the sonic velocities c_l (longitudinal) and c_t (transverse).

In retrospect it has now become clear how the aspects of ref. 1 having to do with bulk moduli and sonic velocities are in need of correction to make them more accurate and convincing. The purpose of this communication is to report improvements that extend the applicability and explanatory power of the scs formulation, *vis-a-vis* semicrystalline polyolefins, and thus enhance its credibility as the binary mixing rule of choice for small-deformation mechanical properties.

2. METHOD

At the time of writing ref. 1, it had not occurred to the author that equation-of-state data for polyethylene melts could be usefully extrapolated to room temperature to obtain a needed estimate for the bulk modulus of the amorphous fraction in the semicrystalline polyethylenes of interest. Thus I overlooked several relevant datasets [8, 9, 10, 11] that should have been taken into account. At the time, I also failed to appreciate the literature's standardization [12, 13] upon pseudo-Tait [14] analysis as the conventional framework for analyzing pressure-volume-temperature data on polymer melts. The development below will show that when observed volume-pressure isotherms are consistently analyzed within the Tait framework, the several available compression dilatometric studies on polyethylene melts and solids fall into much better agreement with the scs than was shown in Fig. 10 of ref. 1. At the same time, however, there arises an apparent disparity between bulk moduli determined by static compression and values derived from ultrasound velocity measurements. Resolution of this disparity, by taking deformation rate effects into account, will be discussed later.

---

[3] $E = 2(1 + \nu)G = 3(1 - 2\nu)K$

2.1 Pseudo-Tait Analysis

The pseudo-Tait equation

$$\rho(P,t) = \frac{\rho(0,t)}{1 - C\ln\left[1 + P/B(t)\right]} \qquad \{1\}$$

or, written as a relative specific volume function,

$$\frac{\rho^{-1}(P,t)}{\rho^{-1}(0,t)} = 1 - C\ln\left[1 + P/B(t)\right] \qquad \{1a\}$$

expresses density (ρ) as a function of temperature (t, in °C) and pressure (P) in terms of of a constant (C) and a temperature-dependent "Tait parameter," $B(t)$. The latter in turn is given by

$$B(t) = b_0 e^{-b_1 t}, \qquad \{2\}$$

where b_0 and b_1 are constants. Equation 2 applies to melts; for the semicrystalline solid case Olabisi and Simha [9] proposed substituting the model

$$B(t) = b_0 - b_1 t, \qquad \{2a\}$$

with suitably adjusted values for b_0 and b_1. For molten polymers, C is often assigned the fixed value 0.0894, but is sometimes allowed to vary as a curve-fitting parameter. Equation 1 becomes a pressure-volume-temperature equation of state upon specifying the low-pressure thermal expansivity, for example as

$$\rho(0,t) = \rho(0,0)e^{-a_0 t}, \qquad \{3\}$$

where α_0 is a temperature-independent value for the thermal expansion coefficient

$$\alpha = \frac{1}{\rho^{-1}} \left.\frac{\partial \rho^{-1}}{\partial t}\right|_P. \qquad \{4\}$$

In practice there is negligible difference between $\rho(P,t)|_{P\,=\,0}$ and $\rho(P,t)|_{P\,=\,1\ \mathrm{atm}}$ for present purposes; thus, to ignore the distinction, the notation $\rho_0(t)$ will be substituted for $\rho(P \leq 1\ \mathrm{atm},t)$. The constant-temperature pressure derivative of the density, known as the compressibility (β), is the reciprocal of the bulk modulus (K), or modulus of compressibility; thus

$$K^{-1} = \beta = \rho^{-1} \left.\frac{\partial \rho}{\partial P}\right|_t. \qquad \{5\}$$

By combining Eqs. 1 and 5 it it is easily shown that the isothermal modulus of compressibility at low pressure reduces to the following simple expression involving the Tait parameters:

$$K(0,t) = B(t)/C. \qquad \{6\}$$

Rearrangement of Eq. 6 and insertion into 1a gives

$$\frac{\rho^{-1}(P,t)}{\rho^{-1}(0,t)} = 1 - C\ln\left[1 + \frac{P}{CK_0(t)}\right]. \qquad \{1b\}$$

(The same notational simplification as described above for density will apply to K's, that is, $K_0(t)$ will mean $K(P \leq 1\text{ atm},t)$. Hence, to determine low-pressure isothermal bulk moduli, one fits isotherms of relative specific volumes vs. pressures with Eq. 1b, using conventional nonlinear least-squares.

This procedure is exemplified in Fig. 1, which shows compression isotherms for a pair of solid polyethylenes studied by Hellwege et al. [15] Extrapolation of those isotherms to zero pressure was accomplished in ref. 1 by using smoothing spline fits to the data expressed as $\beta(P)$. That procedure gave numerical results that differ slightly from those obtained by the procedure outlined above. The latter are summarized in Table I. Similarly, the unit-cell specific volume isotherms measured by Miyaji and coworkers [16] using x-ray diffraction by semicrystalline samples under compression lead to somewhat different (lower) bulk moduli for the crystalline phase when analyzed as above than were earlier obtained by fitting compressibilities with a spline. The data and fit are displayed in Fig. 2, and the results are also collected in Table I.

Other results assembled in Tables I and II came from application of the pseudo-Tait model to several sets of data by other authors. In addition to a few room-temperature observations on semicrystalline solids, there are also shown extrapolated bulk modulus results for amorphous material. These were obtained simply by taking published equations of state for the melt (Table II) and evaluating them at 23 °C. The mean of the nine such values listed, 1.84 GPa, coincides exactly with the estimate obtained by Pastine [11] upon correction of Schuyer's [17] extrapolated value (2.0 GPa) for what Pastine says is the adiabatic-isothermal difference to be expected from the respective heat capacities. (This agreement must be largely fortuitous, because Pastine's correction ignores the frequency-dependent contribution of the shear modulus to the sound velocity, which is found in the discussion below to be of significance.) Considering both the extrapolated melt data

and Schuyer's result, there seems to be sufficient evidence to warrant supplanting the larger estimate (2.8 GPa) arrived at in ref. 1.

For the high-density limiting bulk modulus, that of the ideal crystalline phase, it no longer seems justified to retain the estimate (7.75 GPa) utilized in ref. 1, in view of the downward revision described above to the value implied by the x-ray data of Miyaji et al. A reasonable alternative choice might be the K_0 (7.14 GPa) calculated from an empirically based complete compliance matrix for the polyethylene crystal in the companion paper [18] to ref. 1. The remainder of this report pursues the consequences of "recalibrating" the scs model of ref. 1 by substituting 1.84 and 7.14 GPa as the bulk modulus values for the amorphous and crystalline components, respectively, at ambient conditions.

3. RESULTS AND DISCUSSION

3.1 Bulk Moduli

Figure 3 compares the relevant experimental K_0 values from Table I with the scs theoretical curve (as a function of density) recomputed using the revised pure-phase estimates just mentioned. There is clearly a much more robust match between the data and the model here than in the original work (Fig. 10 of ref. 1). Furthermore, the corresponding alterations to the scs $E(\rho)$ and $G(\rho)$ functions turn out to be virtually imperceptible, so that the main conclusions of refs. 1 and 2 regarding applicability to Young's modulus measurements are unaffected. It is important to note that once the curve of Fig. 3 is made to coincide with the calibration points at the ends, there are no further degrees of freedom left with which to force the curve into agreement with the observations. Indeed, that happened as a consequence of the scs form, entirely without intervention. This serves as strong confirmation of the validity of the self-consistent scheme.

3.2 Longitudinal-Wave Sonic Velocities

There now becomes apparent, however, a disparity between bulk modulus values determined in static compression and those inferred from measurements [19, 20] of both c_l and c_t at ultrasonic frequencies. Such a disparity was pointed out for a single material crystallized and measured under high pressure (490 GPa) by Nagata et al. [21] The general situation is depicted in Fig. 4, where

the few ultrasound-based K_0 results available from the literature [1(Table 3), 19, 20] are compared with the results previously shown in Fig. 3. The ultrasound-based K values in Fig. 4 are reckoned [19] to be uncertain by about 4%, and yet they all lie above the scs curve by more than the 10% or less that Pastine [11] estimates should be the likely difference attributable to isothermal vs. adiabatic conditions of measurement. The existence of the disparity is further illustrated in Fig. 5, which indicates measured c_l values from several additional studies [21, 22, 23] that did not report c_t and therefore could not be used to infer elastic constants. Here the unbroken curve depicts the density dependence of longitudinal sonic velocity, $c_l(\rho)$, calculated (ignoring deformation rate effects) according to [24, 25]

$$c_l = \sqrt{(K + 4G/3)/\rho}\,, \qquad \{7\}$$

where K and G are (static, isothermal) scs values (i.e., values based on data obtained under static or near-static conditions). Again, if the sonic velocity data are in error by no more than 5%, the disparities are clearly significant. They are not, however, unexpected.

Discussions by Pastine [11] and by Hartmann and Jarzynski [19] both teach that the effective value of K should be larger for ultrasound propagation, an adiabatic process, than for static compression, an isothermal one; and Pastine estimates the magnitude of the difference to be of the order of 10%. Furthermore it is well known [26] that, at low frequencies, the storage component (G') of the complex shear modulus for a rubbery amorphous polymer is a strongly increasing function of oscillatory shearing frequency. Thus it is natural to expect this dependence to be reflected in c_l, if G is made correspondingly frequency dependent in Eq. 7.

Unfortunately, it is beyond the scope of the present development to provide a rigorous frequency-dependent theoretical alternative to Eq. 7. Instead, a simple empirical correction scheme for shifting the $c_l(\rho)$ curve to coincide with ultrasound measurements will be proposed here. The empirical corrections introduced will be shown to be of entirely plausible magnitudes, but the derivation of a theoretical model justifying the form of the corrections will not be undertaken.

We proceed by rewriting Eq. 7, as presaged by the discussion just above, in the generalized form

$$c_l = \sqrt{(kK + 4gG/3)/\rho}\,, \qquad \{7a\}$$

where k and g are, respectively, correction factors to account for the effects of cyclic adiabatic compression-dilation and the frequency dependence of the shear modulus. Following the suggestions [11, 19] in the literature, we take k to be a constant with the value 1.1. We then explore what g must be like in order to reproduce observed c_l values from the literature. For this purpose perhaps the largest relevant body of data is that of Piché, [23] who found that polyethylenes with densities between 0.915 and 0.965 g/cm^3 had $c_l(\rho)$ values (measured at 3 MHz) closely following the empirical correlation

$$c_l = a + b(\rho - \rho_a), \qquad \{8\}$$

with a = 1363 m/s, b = 10.32(10^3) (m/s)/(g/cm^3), and the room-temperature amorphous density ρ_a = 0.852 g/cm^3. Equating the right-hand sides of Eqs. 7a and 8 and solving (numerically) for $g(\rho)$ leads to the results plotted in Fig. 6. These results are well represented, over Piché's experimental density range, by the following simple (curve-fit) function of G:

$$g(\rho) = g(G_{\mathrm{scs}}(\rho)) = 304/G_{\mathrm{scs}}^{0.8}, \qquad \{9\}$$

where G_{scs} is in MPa and g is dimensionless. By substituting from Eq. 9 into 7a, we obtain a $c_l(\rho)$ curve empirically shifted from the static scs case to an ultrasonic measurement frequency of 3 MHz. In Fig. 7, this is now added to what was previously shown in Fig. 5, and, necessarily, the match to Piché's correlation is very good. But Fig. 7 also shows Eq. 7a, with g given by Eq. 9, extrapolated well beyond Piché's lower experimental density limit, all the way to the pure-amorphous phase density. This constitutes a prediction that room-temperature c_l values for polyethylenes of very low densities (< 0.9 g/cm^3) will lie well above the linear extension of Piché's correlation. The author is aware of almost no c_l data on polyethylenes in this density range, by which the prediction could be tested. In fact, it appears that the only available data point is one derived by extrapolation to room temperature (Fig. 8) of $c_l(t)$ data obtained on melts by Eby. [22] This point is included in Fig. 7, and it falls remarkably close to the extrapolated prediction at the low end of the possible density range.

There now remains the question of whether or not the empirical shear-modulus correction factors given by Eq. 9 are at all plausible. At the low-density extreme, the value of g given by Eq. 9 is 237; from there it declines monotonically to unity at a density indistinguishable from that of the crystalline phase ($\rho_c \approx 1.01$ g/cm^3). [1] It seems quite plausible to expect that fully crystalline material would require no correction, so we need only to consider whether or not a correction factor as large as 237 is within reason for amorphous material. This is easily answered by inspection of Fig. 9. This shows G' measurements made on the melt of an archetypal high-density polyethylene using a dynamic rheometer, shifted to room temperature according to the usual WLF time-temperature superposition method. [26] Obviously G' increases by more than two orders of magnitude within four decades of relatively low frequencies, and would tend to level off toward the MHz range. Thus a limiting g value as large as given by Eq. 9 is easily justified.

3.3 Transverse-Wave Sonic Velocities

If it is correct to shift from Eq. 7 to 7a using Eq. 9, then Eq. 9 should also be usable to account for the effect of frequency on shear-wave or transverse sonic velocities, c_t. Thus instead of [24, 25]

$$c_t = \sqrt{G/\rho} \qquad \{10\}$$

with G equal to the static scs value, we would now expect c_t to be given by

$$c_t = \sqrt{gG/\rho}\,, \qquad \{10a\}$$

with the same $g(\rho)$ given by Eq. 9. Unfortunately, literature data with which to assess this formulation are very scarce indeed, apparently because strong absorption renders the measurements rather difficult to make. Nevertheless, the few reported results are compared with the unshifted and shifted curves (Eqs. 10 and 10a) in Fig. 10. Again all of the data lie above the uncorrected scs predictions. The observations appear to vary rather less systematically with density alone than was the case with the collected c_l data, but two of the measurements are in very good agreement with the shifted prediction. There are probably very good reasons for the apparent scatter of the data in Fig. 10, but for now it will only be concluded that, clearly, additional

experimental work is needed to elucidate the relation between c_t and the scs elastic constants, especially in the area of very low densities.

3.4 Extensional-Wave Sonic Velocities

A third variant of sonic velocity measurement in need of reconciliation with scs elastic constants is a technique utilizing resonance of a low frequency in a slender rod so that only stretching waves exist. Thus what is measured is the extensional velocity c_e, which depends only upon the Young's modulus and the density. [25] If the experimental conditions satisfy certain assumptions, c_e is given by a simple analog of Eq. 10:

$$c_e = \sqrt{E/\rho}. \qquad \{11\}$$

It is sometimes stated [25] that the criterion that must be met by the experimental conditions in order for Eq. 11 to be valid is that the lateral dimension of the rod under test must be small by comparison with the wavelength of the sound at the measurement frequency. Morse [24(Eq. 7.43)] derives a more rigorous stipulation involving the angular frequency ω of the sound-wave motion, the radius r of the rod, the density, and the shear modulus, viz.

$$c_e = \sqrt{E/\rho} \text{ if } \rho\omega^2 r^2/G << 1 \qquad \{11a\}$$

Morse did not provide specific quantitative guidance on what is meant, in this context, by "<< 1."

A venerable study based on Eq. 11 is that of Davidse, Waterman, and Westerdijk [27] ("DWW"), who reported a sizable set of (c_e, ρ) data measured at kHz frequencies in cylindrical polyethylene rods 10 cm long and 0.6 cm in diameter. Their wavelength was 20 cm, so the lateral dimension-to-wavelength ratio was 0.03, which they took to be small enough to justify reporting Young's moduli obtained from the inverse of Eq. 11,

$$E = \rho c_e^2. \qquad \{11b\}$$

It will be shown below that they evidently did not, however, take into account the effects of small values of G in the inequality attached to Eq. 11a.

Davidse and coworkers themselves compared their Young's moduli obtained from Eq. 11 with measurements they made by conventional slow unidirectional deformation techniques. They noted a disparity amounting to a factor of about 3, but essentially shrugged off this difference as

attributable to inadequacies in the standard methods (flexural and tensile deformations). Surprisingly, their results appear to have been uncritically accepted and repeatedly quoted in review literature [25, 28] for more than a third of a century.

In Fig. 11 are plotted the experimental c_e results of Davidse et al., in comparison with $c_e(\rho)$ computed from Eq. 11 with $E(\rho)$ taken from the present scs model. In Fig. 12, the same comparison is shown in terms of E vs. density, and here the flexural and tensile modulus results originally reported for a few of the same materials are included. To Fig. 12 has also been added the locus of the Hashin-Shtrickman upper bound [1, 29] corresponding to the scs model. Many of the reported c_e-based Young's modulus points lie above this bound, indicating a disparity that demands to be taken seriously.

A striking reconciliation of the DWW data with the scs model has been found which is somewhat like the empirical shifting approach utilized above, but which proceeds by a very different route. Instead of just solving for a "fudge factor" (however plausible) that will remove the disparity, let us regard the ratio $\rho\omega^2 r^2/G$ in Morse's inequality as a <u>measure</u> of how much the DWW experimental conditions depart from satisfying the criterion for Eq. 11 to be valid. Fortunately, DWW tabulate everything needed to compute this ratio for each of their experiments, except for G, but surely a good estimate of G in each case is $G_{\mathrm{scs}}(\rho)$, so that will be used. And then let us see how the ratio correlates with the departure of the E's according to Eq. 11b from the corresponding scs values; that is, let us look at $\rho c_e^2/E_{\mathrm{scs}}(\rho)$ vs. $\rho\omega^2 r^2/G_{\mathrm{scs}}(\rho)$. Figure 13 depicts the relationship between these two quantities. What appears there is a spectacular collapse of the previously unexplained scatter in the ρc_e^2 data! The effect is so dramatic that there can be little doubt of the validity of the implied correction, namely

$$E(c_e) = \rho c_e^2/\max(1,y) \text{ where } y = 0.08222 + 37.28\rho\omega^2 r^2/G_{\mathrm{scs}}(\rho). \qquad \{12\}$$

The fitted line (y) in Fig. 13 reaches unity at $\rho\omega^2 r^2/G = 0.025$; this then is the value to be taken as the concrete numerical limit in Morse's criterion for the validity of Eq. 11 without correction. That is, this analysis implies, instead of 11a,

$$c_e = \sqrt{E/\rho} \text{ if } \rho\omega^2 r^2/G \leq 0.025. \qquad \{11c\}$$

We can apply the correction in Eq. 12 inversely to obtain corrected c_e values for comparison with the scs predictions based on E_{scs}, as follows:

$$c_e^{\mathrm{corr.}} = c_e / \sqrt{\max(1,y)}, \qquad \{11\mathrm{d}\}$$

where y is the same as in Eq. 12. Figure 11 redrawn with c_e values corrected according to Eq. 11d appears as Fig. 14, for ease of comparison with the original uncorrected DWW results.

4. CONCLUSION

This report has considered two key aspects of the application of the Hill-Budiansky-Berryman "self-consistent" mechanical properties mixing model to the case of isotropic polyethylenes of varying crystalline content, and hence density, at ambient conditions. Compressibility modulus estimates for the amorphous and crystalline phases were revised downward from those used in earlier work with this model. After these revisions, the scs predictions of sound propagation speeds do not match measured values unless allowance is made for effects of deformation rate (i.e., frequency) or, in the instance of extensional waves, for mismatch between measurement conditions and theoretical assumptions made in the data analysis. The main conclusion is that, for the materials discussed, the scs remains viable under Hildebrand's tenet quoted in the prologue: It is "[a] model that is consistent with all properties, even if only approximately, [and] can probably be made more precise ..."

An eventual implication of this work that some will no doubt find unpalatable, if the scs continues to prove successful in rationalizing additional data, is as follows: Once the elastic constants, yield stresses and strains, and sound propagation velocities have been accounted for to within experimental uncertainties by the two-phase self-consistent model, it follows that it will be fruitless to seek evidence of higher-order phenomena attributable to "rigid amorphous material," "interphases," and so forth, in the sort of small-deformation experimental data as are routinely available.

ACKNOWLEDGEMENT

The author thanks Mr. Dale L. Embry for calling attention to relevant material in ref. 14.

REFERENCES

1. Jay Janzen, Polym. Eng. Sci. **32:** 1242 (1992)

2. R. Hill, J. Mech. Phys. Solids **13:** 213 (1965)

3. B. Budiansky, J. Mech. Phys. Solids **13:** 223 (1965)

4. James G. Berryman, Appl. Phys. Lett. **35:** 856 (1979)

5. Jay Janzen and David F. Register, "Crystallinity dependence of modulus and yield properties in polyethylenes," SPE 54th annual technical conference, Indianapolis, Indiana (1996)

6. Richard A. Beth, "Statics of elastic bodies," in *Handbook of Physics*, E. U. Condon and Hugh Odishaw, Ed. (McGraw-Hill, New York, 1958), pp. 3-64¾3-77

7. Herbert L. Anderson, "Practical physics [Section 1.08]," in *Physics Vade Mecum*, Herbert L. Anderson, Ed. (American Institute of Physics, New York, 1981), pp. 40-45

8. Paul Zoller, J. Appl. Polym. Sci. **23:** 1051 (1979)

9. Olagoke Olabisi and Robert Simha, Macromolecules **8:** 206 (1975)

10. S. Beret and J. M. Prausnitz, Macromolecules **8:** 536 (1975)

11. D. John Pastine, J. Chem. Phys. **49:** 3012 (1968)

12. Paul Zoller, "PVT relationships and equations of state of polymers," in *Polymer Handbook*, J. Brandrup and E. H. Immergut, Ed. (Wiley, New York, 1989), pp. VI/475-483

13. Robert A. Orwoll, "Densities, coefficients of thermal expansion, and compressibilities of amorphous polymers," in *Physical Properties of Polymers Handbook*, James E. Mark, Ed. (American Institute of Physics, Woodbury, New York, 1996), pp. 81-89

14. J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworth, London, 1969), pp. 26-31

15. Von K.-H. Hellwege, W. Knappe, and P. Lehmann, Kolloid-Z. Z. Polym. **183:** 110 (1962)

16. Hideki Miyaji, Takanao Asahi, Yoshihisa Miyamoto, and Kenjiro Asai, J. Polym. Sci., Polym. Phys. Ed. **25:** 159 (1987)

17. J. Schuyer, J. Polym. Sci. **36:** 475 (1959)

18. Jay Janzen, Polym. Eng. Sci. **32:** 1255 (1992)

19. Bruce Hartmann and Jacek Jarzynski, J. Acoust. Soc. Amer. **56:** 1469 (1974)

20. N. Lagakos, J. Jarzynski, J. H. Cole, and J. A. Bucaro, J. Appl. Phys. **59:** 4017 (1986)

21. Kiofumi Nagata, Katsuharu Tagashira, Seiji Taki, and Tetuo Takemura, Jpn. J. Appl. Phys. **19:** 985 (1980)

22. R. K. Eby, J. Acoust. Soc. Amer. **36:** 1485 (1964)

23. L. Piché, Polym. Eng. Sci. **24:** 1354 (1984)

24. Philip M. Morse, "Vibrations of elastic bodies; wave propagation in elastic solids," in *Handbook of Physics*, E. U. Condon and Hugh Odishaw, Ed. (McGraw-Hill, New York, 1958), pp. 3-97¾3−111

25. Bruce Hartmann, "Acoustic properties," in *Physical Properties of Polymers Handbook*, James E. Mark, Ed. (American Institute of Physics, Woodbury, New York, 1996), pp. 677-686

26. John D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (John Wiley & Sons, New York, 1980), pp. 264-280, 368

27. P. D. Davidse, H. I. Waterman, and J. B. Westerdijk, J. Polym. Sci. **59:** 389 (1962)

28. D. W. Phillips and R. A. Pethrick, J. Macromol. Sci.—Rev. Macromol. Chem. **C16:** 1 (1978)

29. J. Peter Watt, Geoffrey F. Davies, and Richard J. O'Connell, Rev. Geophys. Space Phys. **14:** 541 (1976)

Table I.† collected bulk modulus results for polyethylene solids at room temperature

source (data/report) ref.	sample	t °C	$\rho_0(t)$ g/cm³	maximum pressure MPa	Fig. 3 ident.	b_0 MPa	b_1 MPa/°C	C ¾	B(23 °C) MPa	K_0(23 °C) GPa
[Table II]	amorphous mean	23	0.8520	¾	m	¾	¾	¾	¾	1.84
15/this work	Lupolen 1811 H	19.4	0.9183	200	h	¾	¾	0.0894[f]		2.47
15/Fig. 1	Lupolen 1811 H	19.4	0.9183	200		¾	¾	0.0890[v]		2.46
15/9	Lupolen 1811 H	19.4	0.9183	200		275.8	1.7442	0.0894[f]	235.68	2.64
9/9	HMLPE	20	0.9268	200	os	305.1	1.4765	0.0894[f]	271.14	3.03
9/9	BPE	20	0.9320	200	os	323.3	2.2651	0.0894[f]	271.20	3.03
30/11	Alathon 7020	25	0.954	1621	wp	¾	¾	¾	¾	3.86
15/this work	Marlex 9	20	0.9728	200	h	¾	¾	0.0894[f]		4.52
15/Fig. 1	Marlex 9	20	0.9728	200		¾	¾	0.0612[v]		4.09
15/9	Marlex 9	20	0.9728	200		447.9	2.1720	0.0894[f]	397.95	4.45
9/9	LPE	20	0.9794	200	os	475.8	2.2702	0.0894[f]	423.59	4.74
16/this work	Sholex 6009	25	0.9994	1800	xm	¾	¾	0.0894[f]		5.44
16/Fig. 2	Sholex 6009	25	0.9997	1800		¾	¾	0.0940[v]		5.64
11/this work	crystal	25	0.9968	5200, theory		¾	¾	0.0894[f]		5.95
31/1&18	DA	20	1.0019	785	xi	¾	¾	¾	¾	6.40
18/18	crystal	23	1.0117	¾	j	¾	¾	¾	¾	7.14

† b_0 and b_1 are for use in eq. 2a.
[f] fixed
[v] varied

Table II.* pseudo-Tait analysis results for polyethylene melts

source (data/analysis) ref. no.	sample	t °C	$\rho_0(t)$ g/cm³	maximum pressure MPa	b_0 kg/cm²	b_0 MPa	b_1 °C⁻¹	C ¾	B(23 °C) MPa	K_0(23 °C) GPa
8/8	A	23	0.917	196	1968	193.0	$4.7005(10^{-3})$	0.0894[f]	173.22	1.94
8/8	C	23	0.917	196	1904	186.7	$4.3914(10^{-3})$	0.0894[f]	168.78	1.89
8/8	B	23	0.918	196	2005	196.6	$4.6005(10^{-3})$	0.0894[f]	176.88	1.98
15/9	Lupolen 1811 H	19.4	0.9183	200		187.9	$4.796(10^{-3})$	0.0894[f]	168.28	1.88
10/10	PE	25	0.92	100		198.73	$5.0976(10^{-3})$	0.096959[v]	176.74	1.82
9/9	HMLPE	20	0.9268	200		168.3	$4.292(10^{-3})$	0.0894[f]	152.48	1.71
9/9	BPE	20	0.9320	200		177.1	$4.699(10^{-3})$	0.0894[f]	158.96	1.78
15/9	Marlex 9	20	0.9728	200		173.8	$4.558(10^{-3})$	0.0894[f]	156.50	1.75
9/9	LPE	20	0.9794	200		176.7	$4.661(10^{-3})$	0.0894[f]	158.74	1.78
mean										1.84

* b_0 and b_1 are for use in eq. 2.
[f] fixed
[v] varied

Figure 1

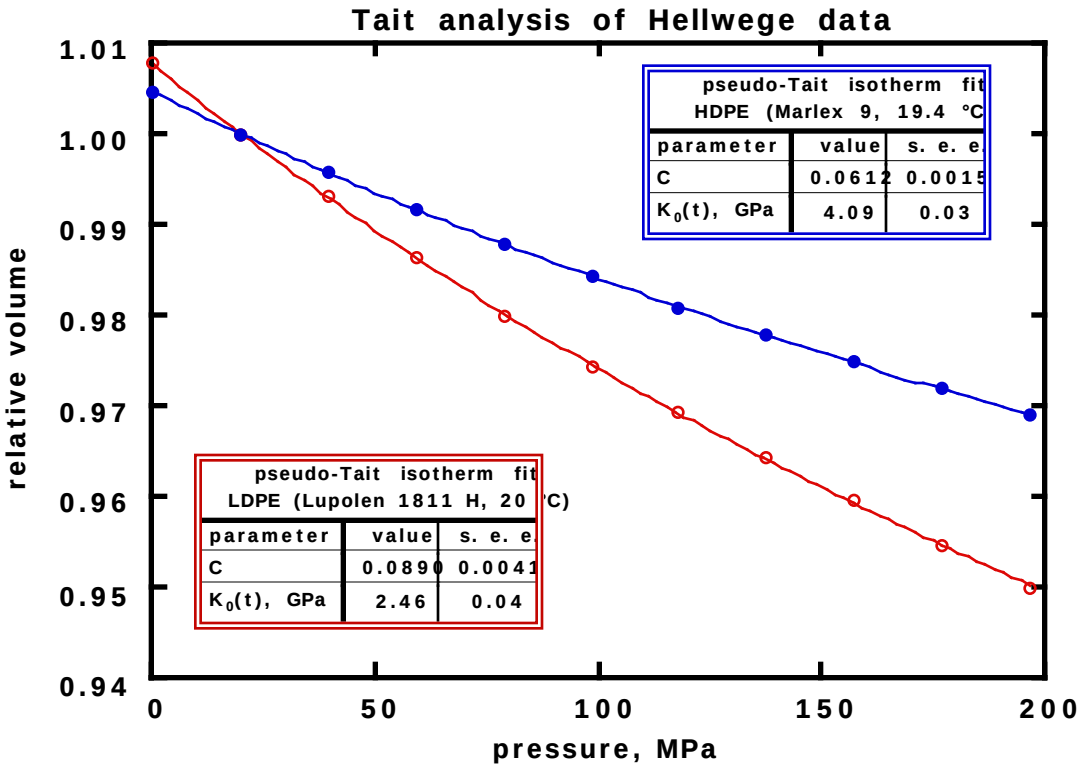

Tait analysis of Hellwege data
relative volume
pressure, MPa
1.01
1.00
0.99
0.98
0.97
0.96
0.95
0.94
0
50
100
150
200
pseudo-Tait isotherm fit
HDPE (Marlex 9, 19.4 °C
parameter | value | s. e. e
C | 0.0612 | 0.0015
K0(t), GPa | 4.09 | 0.03
pseudo-Tait isotherm fit
LDPE (Lupolen 1811 H, 20 °C)
parameter | value | s. e. e
C | 0.0890 | 0.0041
K0(t), GPa | 2.46 | 0.04

Figure 2

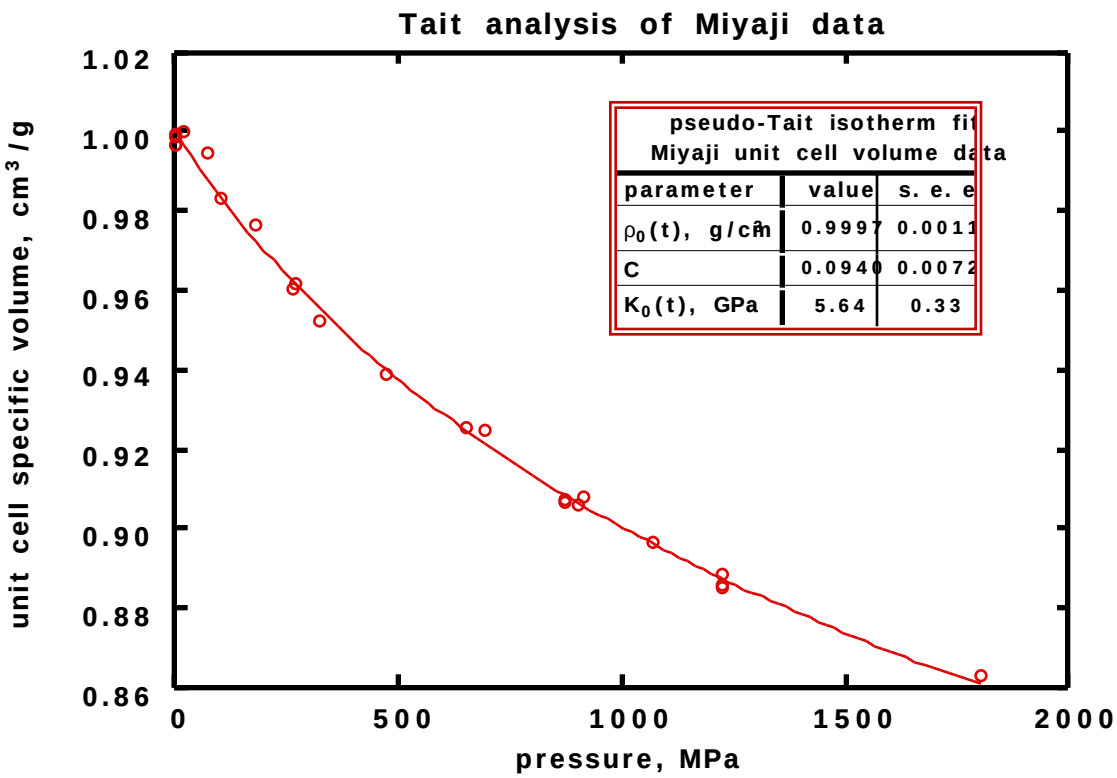

Tait analysis of Miyaji data
unit cell specific volume, cm³/g
1.02
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0
500
1000
1500
2000
pressure, MPa
pseudo-Tait isotherm fit
Miyaji unit cell volume data
parameter | value | s. e. e
ρ0(t), g/cm3 | 0.9997 | 0.0011
C | 0.0940 | 0.0072
K0(t), GPa | 5.64 | 0.33

Figure 3

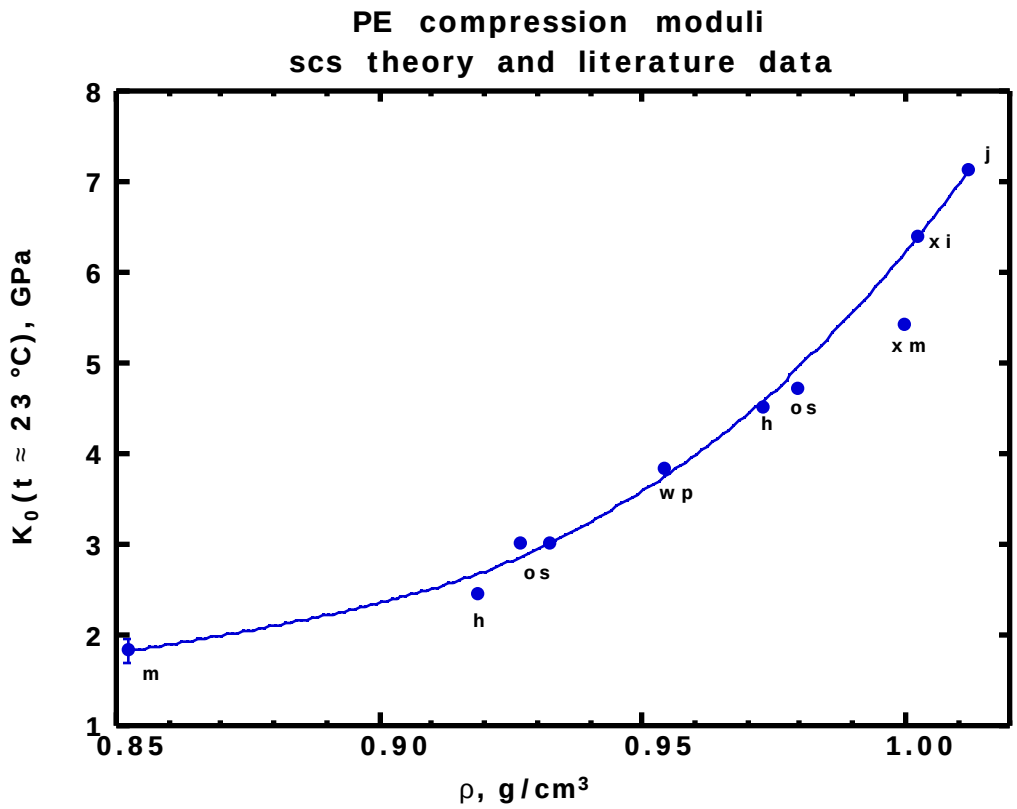

PE compression moduli
scs theory and literature data
K0 (t ≈ 23 °C), GPa
ρ, g/cm3
0.85
0.90
0.95
1.00
1
2
3
4
5
6
7
8
m
h
o s
w p
h
o s
x m
x i
j

Figure 4

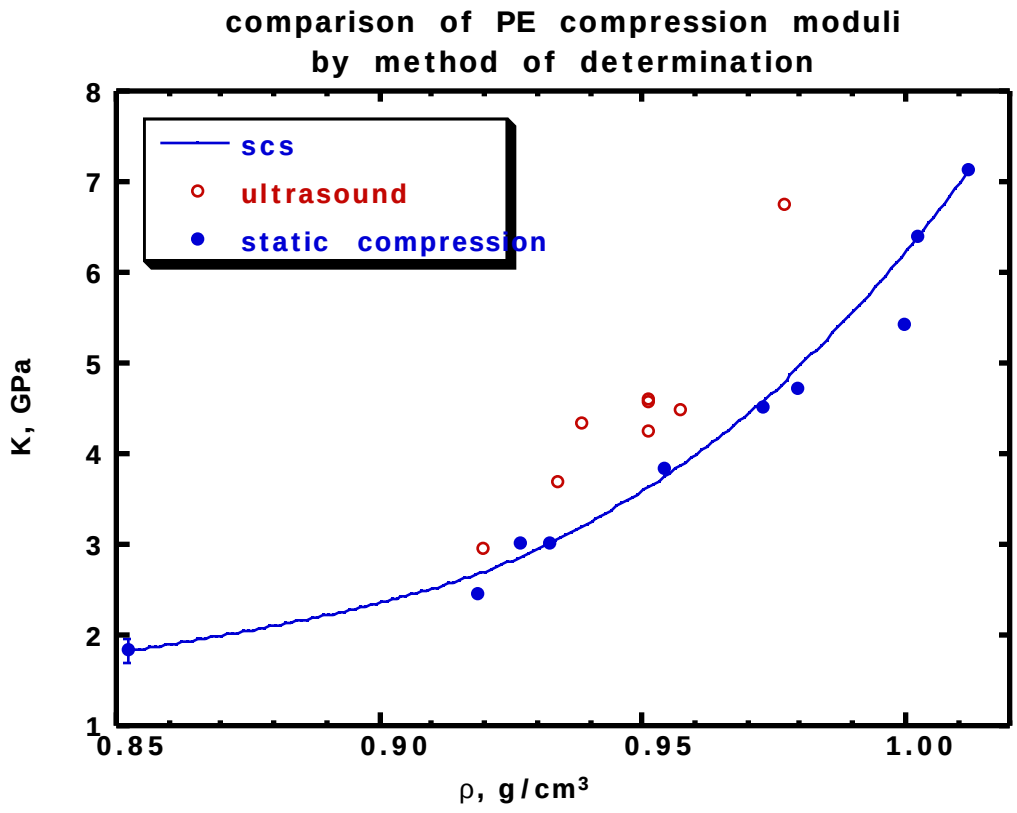

comparison of PE compression moduli
by method of determination
scs
ultrasound
static compression
K, GPa
ρ, g/cm³
8
7
6
5
4
3
2
1
0.85
0.90
0.95
1.00

Figure 5

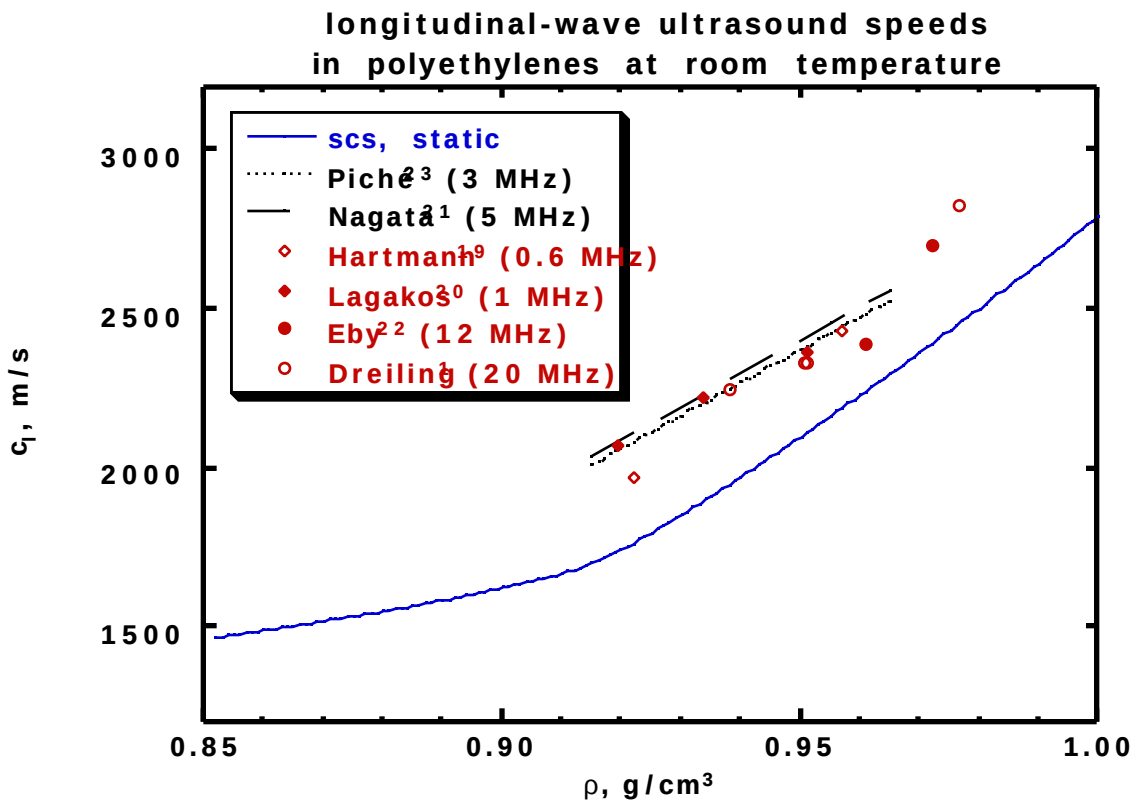

longitudinal-wave ultrasound speeds
in polyethylenes at room temperature
scs, static
Piché[23] (3 MHz)
Nagata[21] (5 MHz)
Hartmann[19] (0.6 MHz)
Lagakos[20] (1 MHz)
Eby[22] (12 MHz)
Dreiling[1] (20 MHz)
3000
2500
2000
1500
c_l, m/s
0.85
0.90
0.95
1.00
ρ, g/cm³

Figure 6

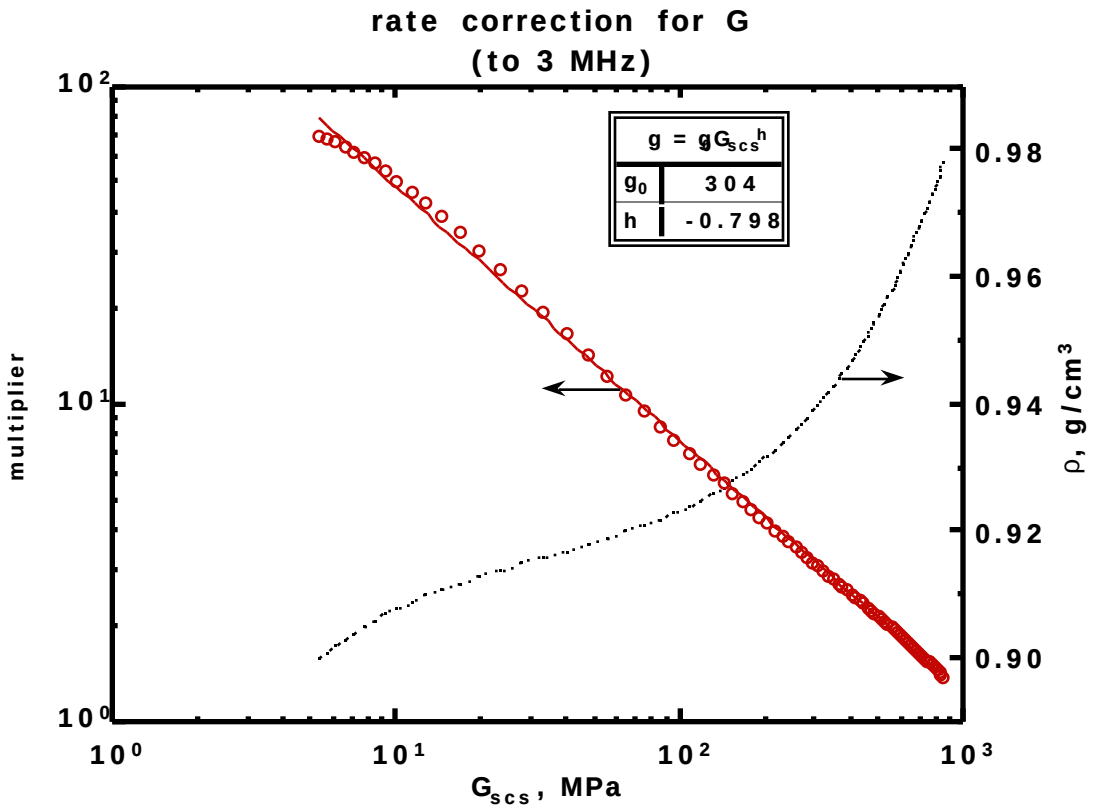

rate correction for G
(to 3 MHz)
g = g0Gscs^h
g0 304
h -0.798
multiplier
ρ, g/cm3
Gscs, MPa
10^0
10^1
10^2
10^3
0.90
0.92
0.94
0.96
0.98

Figure 7

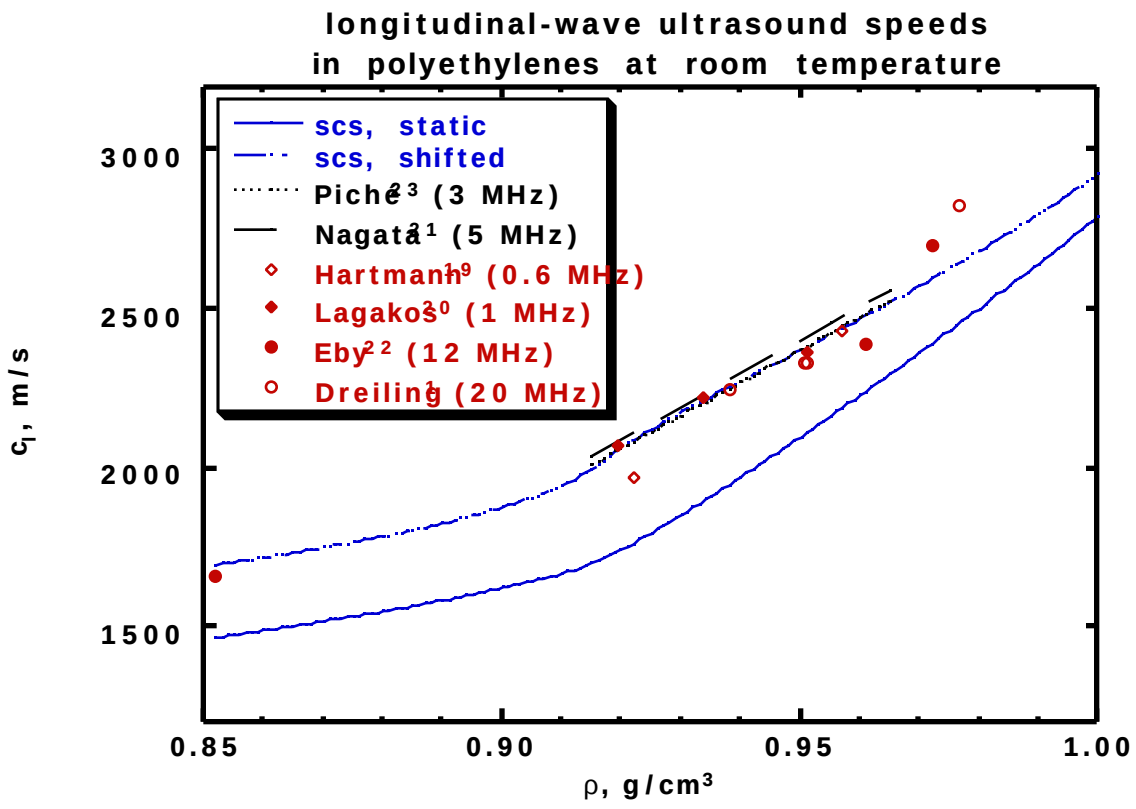

longitudinal-wave ultrasound speeds
in polyethylenes at room temperature
scs, static
scs, shifted
Piché[23] (3 MHz)
Nagata[21] (5 MHz)
Hartmann[19] (0.6 MHz)
Lagakos[20] (1 MHz)
Eby[22] (12 MHz)
Dreiling[1] (20 MHz)
3000
2500
2000
1500
c_l, m/s
0.85
0.90
0.95
1.00
ρ, g/cm³

Figure 8

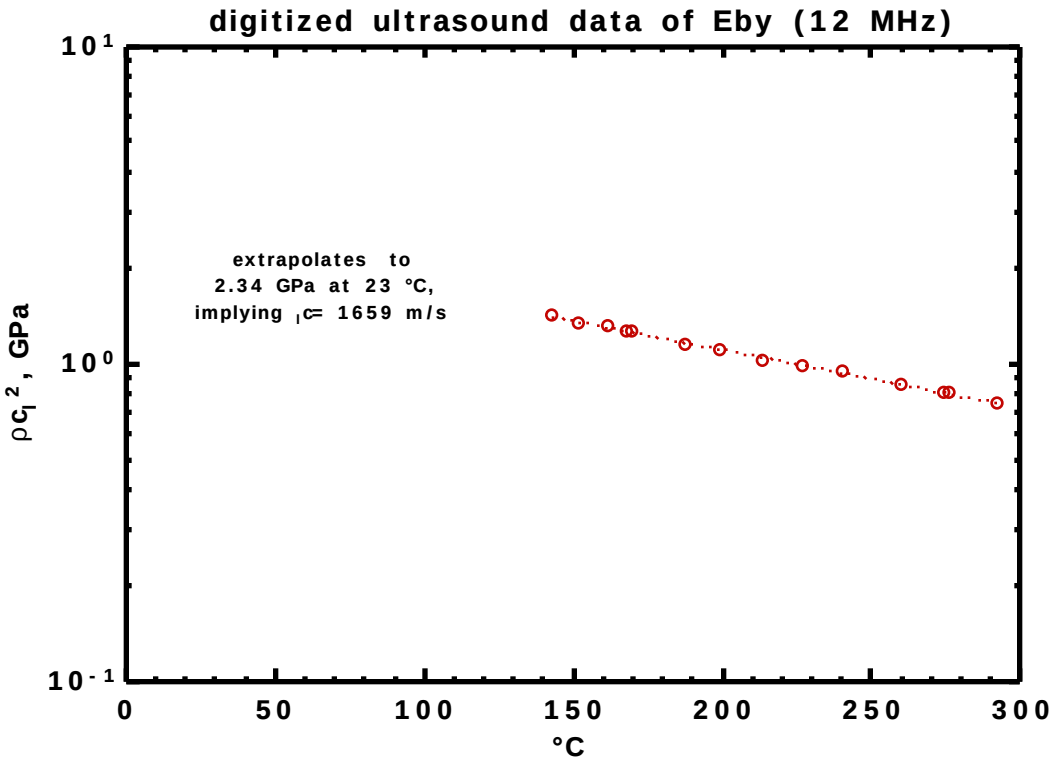

digitized ultrasound data of Eby (12 MHz)
extrapolates to
2.34 GPa at 23 °C,
implying $_l c$= 1659 m/s
ρc_l^2, GPa
10^1
10^0
10^{-1}
0
50
100
150
200
250
300
°C

Figure 9

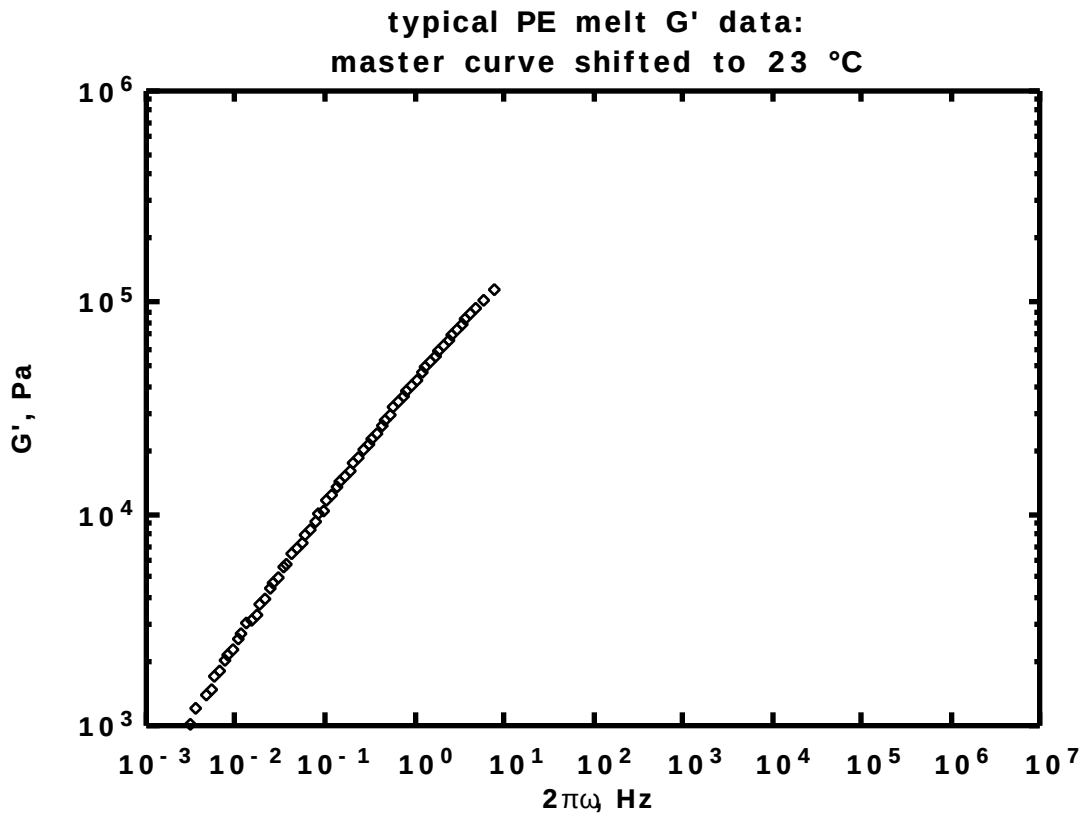

typical PE melt G' data:
master curve shifted to 23 °C
G', Pa
10^6
10^5
10^4
10^3
10^-3 10^-2 10^-1 10^0 10^1 10^2 10^3 10^4 10^5 10^6 10^7
2πω, Hz

Figure 10

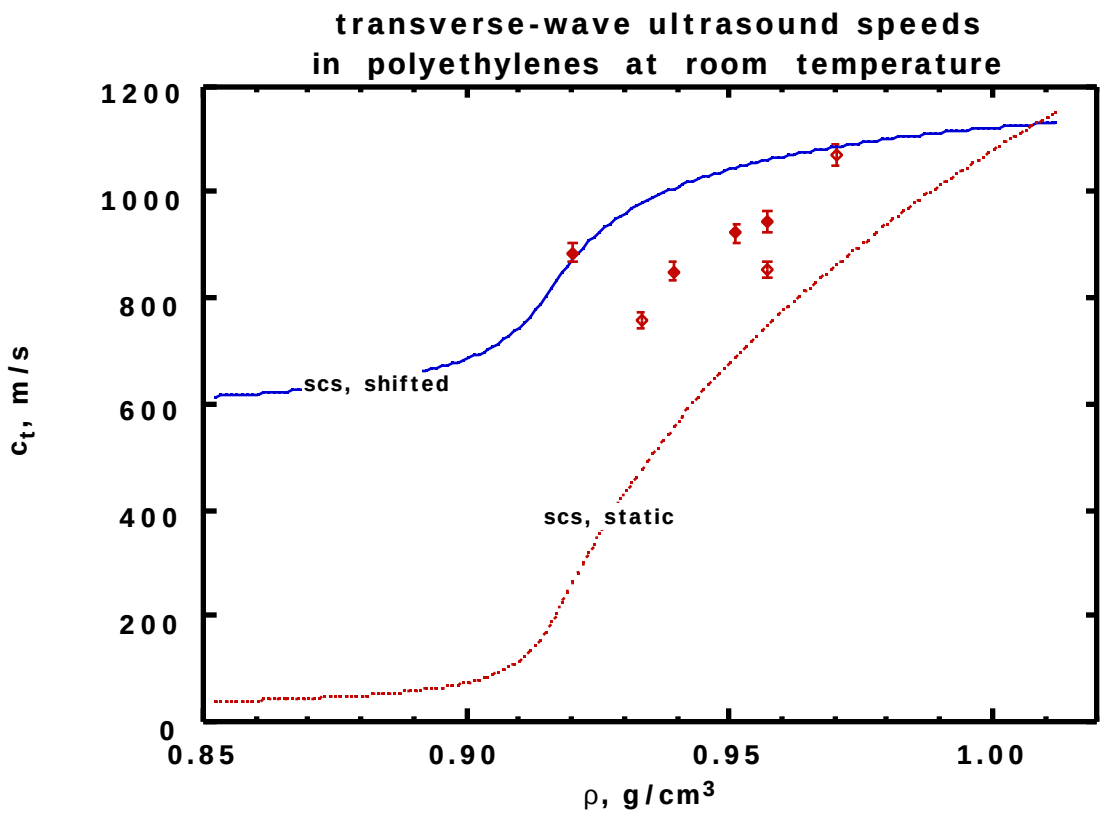

transverse-wave ultrasound speeds
in polyethylenes at room temperature
1200
1000
800
600
400
200
0
0.85
0.90
0.95
1.00
c_t, m/s
ρ, g/cm³
scs, shifted
scs, static

Figure 11

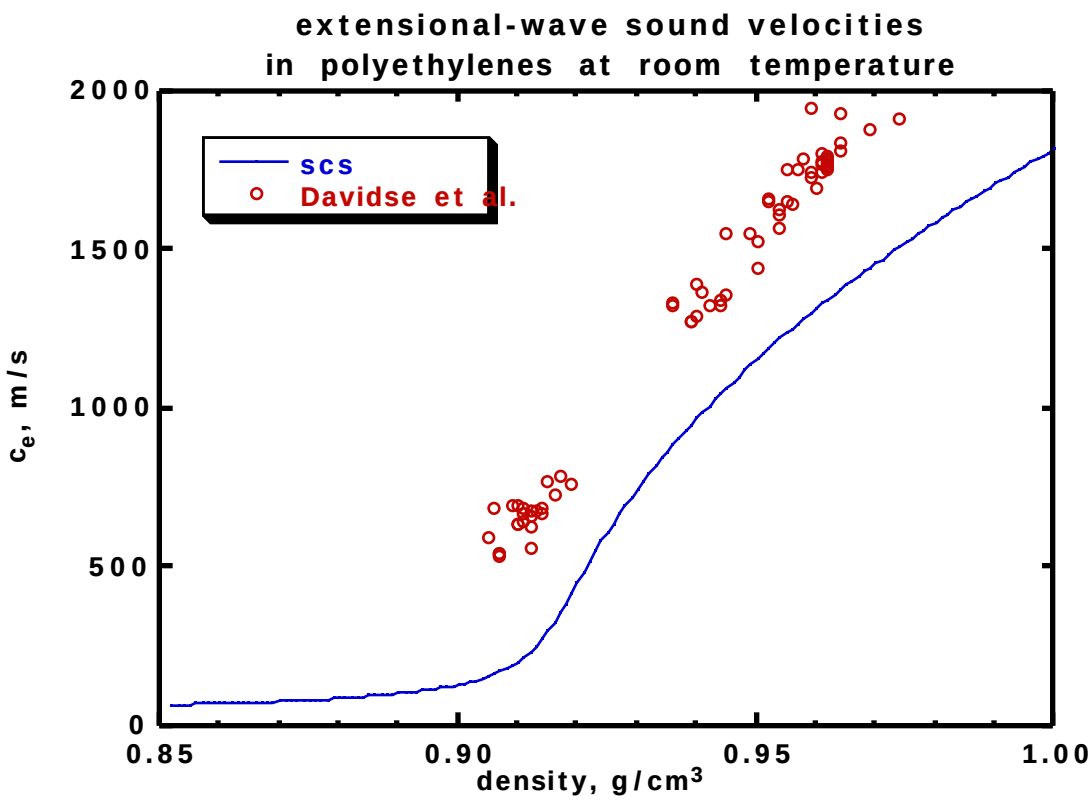

extensional-wave sound velocities
in polyethylenes at room temperature
scs
Davidse et al.
2000
1500
1000
500
0
0.85
0.90
0.95
1.00
density, g/cm3
ce, m/s

Figure 12

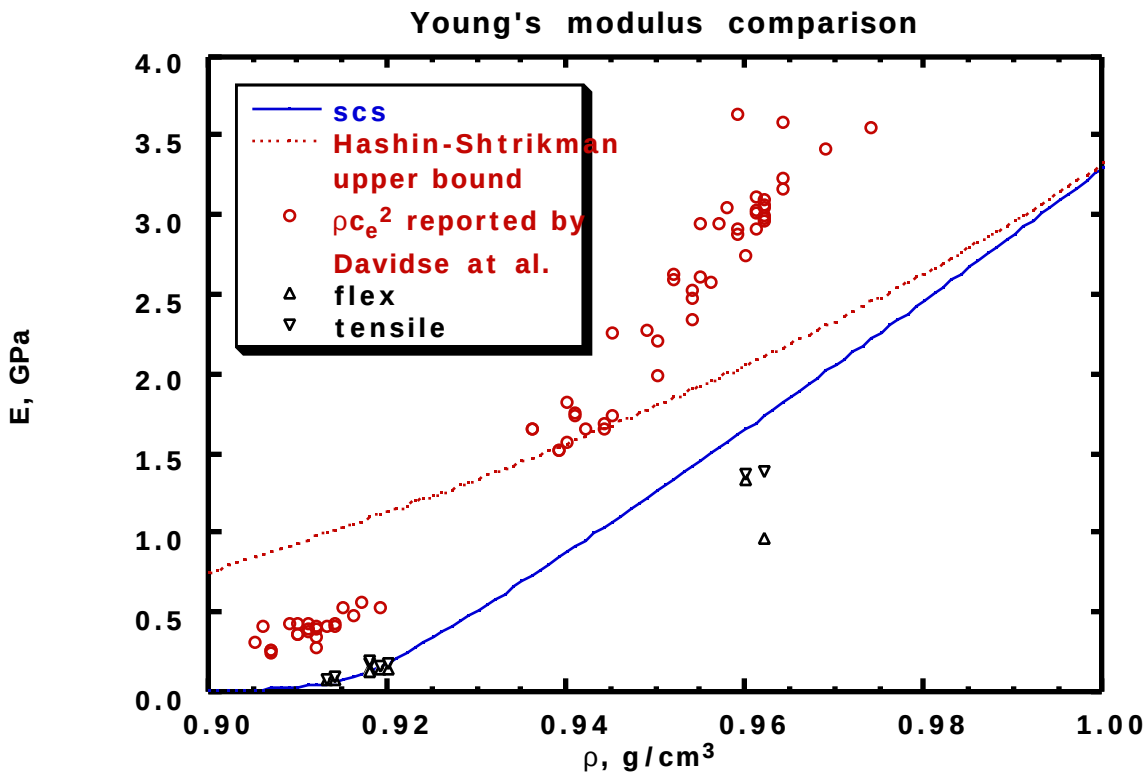

Young's modulus comparison
scs
Hashin-Shtrikman upper bound
ρc_e^2 reported by Davidse at al.
flex
tensile
E, GPa
ρ, g/cm³
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.90
0.92
0.94
0.96
0.98
1.00

Figure 13

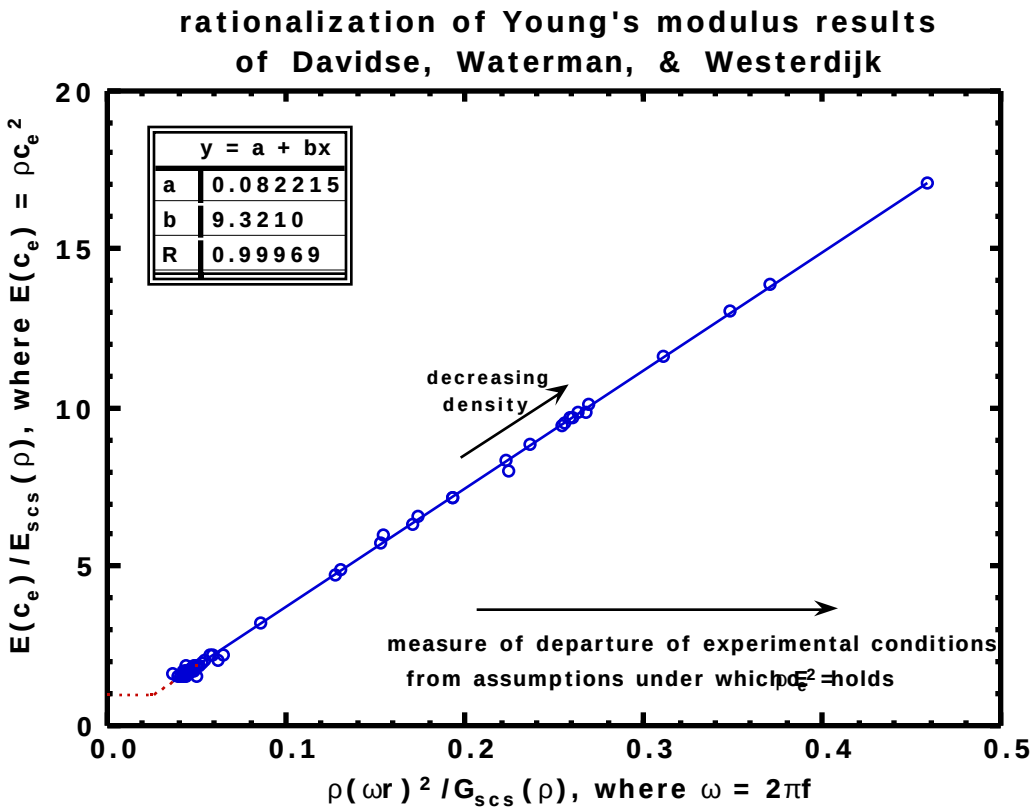
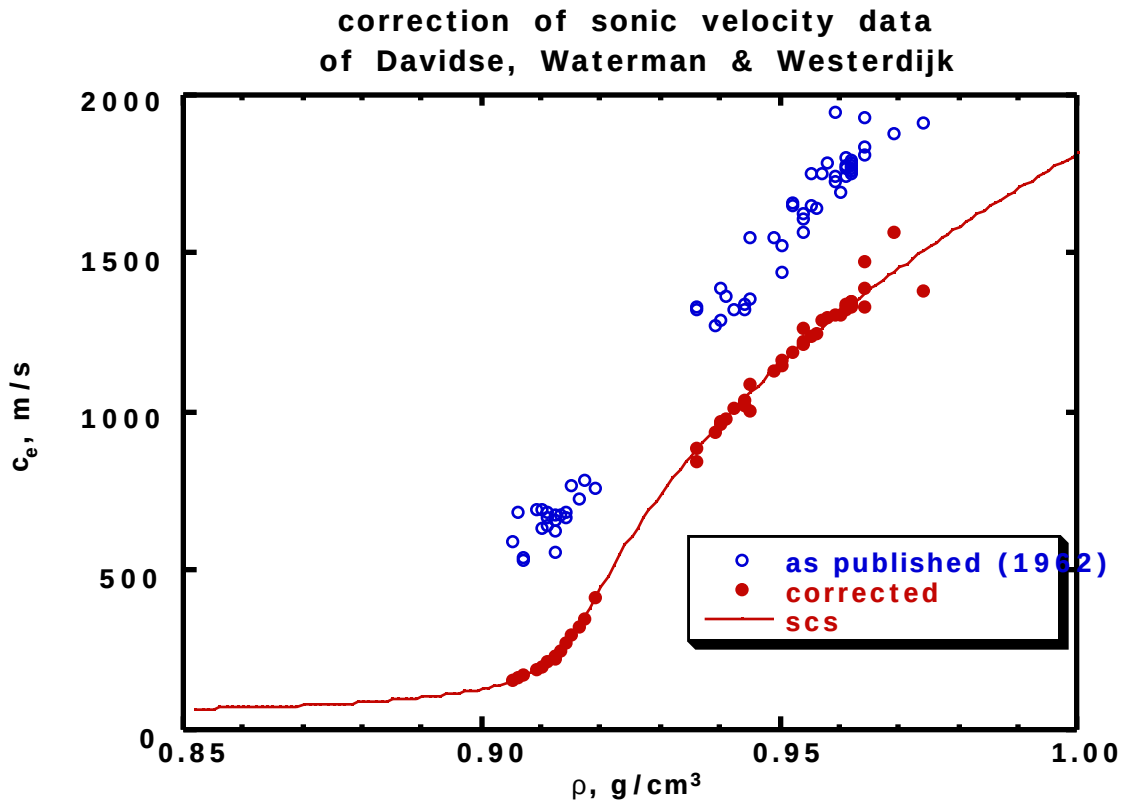

rationalization of Young's modulus results
of Davidse, Waterman, & Westerdijk
y = a + bx
a 0.082215
b 9.3210
R 0.99969
decreasing
density
measure of departure of experimental conditions
from assumptions under which $\rho c_e^2 =$ holds
$E(c_e)/E_{scs}(\rho)$, where $E(c_e) = \rho c_e^2$
$\rho(\omega r)^2/G_{scs}(\rho)$, where $\omega = 2\pi f$
0
5
10
15
20
0.0
0.1
0.2
0.3
0.4
0.5

Figure 14


correction of sonic velocity data
of Davidse, Waterman & Westerdijk
2000
1500
1000
500
0
0.85
0.90
0.95
1.00
c_e, m/s
ρ, g/cm³
as published (1962)
corrected
scs