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Theoretical Interpretation of the Swelling of Elastomers[†]

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ABSTRACT: The swelling dilation moduli reported in the preceding paper are here analyzed with use of a recently proposed theory of rubber elasticity. The theory predicts that the elastic equation of state is dependent on solution thermodynamic parameters, in agreement with the observations. It is successful in accounting for the solvent effects, which is a step forward; it also succeeds in predicting that the Mooney–Rivlin C_2 term decreases with increasing extent of swelling. Unfortunately, agreement with experiment cannot be achieved with a single consistent set of parameters. Further progress on the theory of rubber elasticity is needed to understand the swelling process completely, and a suggestion is made as to where this advance might be found.

Introduction

The underlying principles of the physics of high elasticity are well understood, but there remain several nagging discrepancies between theory and experiment that require resolution before we can claim that we know everything that needs to be know about the subject. Theory cannot yet cope with the whole range of deformations from uniaxial to biaxial extension.[1,2] The sorption measurements reported in the preceding paper[3] (hereafter called paper 1) demonstrate conclusively that one of the basic tenets of the theory, the Flory–Rehner[4] assumption of additivity of mixing and elastic free energies, is incorrect. The evidence for this case has been accumulating since the first sorption experiment of this kind was undertaken by Gee, Herbert, and Roberts.[5] The subsequent experiments performed by Eichinger and co-workers[6-11] have methodically dispensed with potential explanations of the anomalies that might be invoked to preserve Flory–Rehner theory. The results of paper 1 are likewise conclusive in this respect.

A comprehensive theory of elasticity must account for the solvent dependence of the dilation moduli.[3,11] Several well-known elasticity theories, including those devised by Mooney and Rivlin,[12,13] James and Guth,[14] Wall and Flory,[15,16] and Flory and Erman,[17,18] have been compared previously with experimental results from differential swelling experiments, but none of them can account for the solvent effects observed in the experiments. In this paper we present the theoretical predictions of a more recent theory[19] and make comparisons between theoretical predictions and the experimental results.

Review of Network Distribution Theory

It was argued[19] that, because the elastic free energy is no more than about 1% of the total free energy of a typical elastomer, perturbation theory is the proper context in which to formulate elasticity theory. Given partition functions for cross-linked (subscript c) and un-cross-linked (subscript u) polymers in the form

$$Z_c = \exp(-A_c/kT) \quad \text{and} \quad Z_u = \exp(-A_u/kT) \qquad (1)$$

respectively, it follows that one may define the elastic free energy A_{el} as

$$A_{el} = -kT \ln (Z_c/Z_u) \qquad (2)$$

because it is trivially true that $Z_c = Z_u(Z_c/Z_u)$ and hence that $A_c = A_u + A_{el}$. There are no assumptions as to the dependence or independence of A_{el} upon any of the molecular parameters that are involved in the construction of A_u; eqs 1 and 2 are merely formal definitions that constitute the basis of what is to follow. However, you may anticipate that A_u will be given by the theory of linear polymers and their solutions.

Network distribution theory is based on the calculation of the distribution function of the gyration tensor for the elastic body. The basic tenet of this treatment of elasticity is that there is no externally imposed state of strain that is not identical to one that the unfettered elastic body might realize by means of a spontaneous fluctuation away from the unstrained state, which coincides with the most probable configuration. This simple observation immediately dispenses with the need to make assumptions either about the way in which constraints are imposed or about the microscopic relation between molecular deformation and macroscopic strain.

The measure of the state of deformation of the elastic body is contained in the gyration tensor, a 3 × 3 matrix defined solely in terms of the atomic coordinates by

$$S = (N + n_1)\mathbf{YY}' \qquad (3)$$

where N is the number of polymer segments and n_1 is the number of solvent molecules. The matrix $\mathbf{Y} = [X, x]$ (with transpose $\mathbf{Y}'$) is a $3 \times (N + n_1)$ matrix of Cartesian coordinates, X for the polymer segments and x for the solvent coordinates. The free energy that is to be calculated will be a function of S, N, n_1, and T. The tensor S is a generalization of the volume for an anisometric object. (If we were able to formulate the theory for the un-cross-linked system exactly, we should find that the free energy is independent of the shape of the system, except for those configurations that are extremely anisometric and which therefore have a large surface free energy.)

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The total potential energies of the systems (cross-linked and un-cross-linked) consist of separable contributions from bonded and nonbonded interactions, which are denoted by $V(b;X,x)$ and $V(\bar{b};X,x)$, respectively (without subscript, the potential applies to either system and can be made to apply to a particular one upon inserting one of the subscripts c or u). The normalized distribution function of the gyration tensor S is given by

$$P(S)\,\mathrm{d}S = Z^{-1}\,\mathrm{d}S \int \cdots \int \exp\{-(kT)^{-1}[V(b;X,x) + V(\bar{b};X,x)]\}\,\mathrm{d}X\,\mathrm{d}x/\mathrm{d}S \quad (4)$$

for either the cross-linked or the un-cross-linked system. In the integral, we literally mean to divide out the volume element corresponding to the components of the gyration tensor from the total volume element on the configuration space. That one can do this is apparent upon transforming the coordinates to a spherical polar system.[19] In either case, the free energy is given by

$$A = -kT \ln [P(S)] \quad (5)$$

so that the elastic free energy is, to within an additive term independent of the deformation

$$A_{\mathrm{el}} = -kT \ln [P_{\mathrm{c}}(S)/P_{\mathrm{u}}(S)] \quad (6)$$

on combination of eqs 2 and 5.

The value of S that maximizes $P(S)$ and minimizes $A_{\mathrm{el}}(S)$ is $S°$, and it can be obtained by solving the equation $\mathrm{d}P(S)/\mathrm{d}S|_{S=S°} = 0$. The state defined by $S°$ is the unstrained state. Thus, it follows that

$$\Delta A_{\mathrm{el}} = A_{\mathrm{el}}(S) - A_{\mathrm{el}}(S°) = -kT \ln [P_{\mathrm{c}}(S)/P_{\mathrm{c}}(S°)] \quad (7)$$

on the most reasonable assumption, stated above, that the free energy of the un-cross-linked system does not depend on the anisometry of its macroscopic equilibrium configuration and that, therefore, the un-cross-linked system factors out from this equation. Since S and $S°$ are second rank tensors, they are related to one another through the deformation gradient tensor λ by the equation

$$S = \lambda S° \lambda' \quad (8)$$

This definition of strain is macroscopic, and it is made without additional assumptions about isotropy or homogeneity.

Upon integrating over the solvent coordinates, the true potentials for the polymer segments are converted into potentials of mean force, denoted by $\bar{V}$. The bonded potential of mean force can be written as[20,21]

$$\bar{V}(b;X) = kT\gamma\,\mathrm{tr}(XKX') \quad (9)$$

where $\gamma = 3/2\langle l^2\rangle_0$, and $\langle l^2\rangle_0$ is the mean-square length of one statistical bond in a chain. The polymer is thus represented in the Gaussian approximation. The force constant matrix K is a Kirchhoff matrix[22,23] that describes the connectivity of the molecules; for the network K_{c} has but a single zero eigenvalue corresponding to the center of mass motion of the connected network, and for the un-cross-linked reference system, K_{u} is a direct sum of Rouse matrices for the several independent polymer molecules. (Note that there is no assumption that the reference system consists of linear chains, although in most cases it may be convenient to use a linear reference system, even though the actual network of interest might have been synthesized from branched molecules.) Substituting eq 9 into eq 6 one obtains

$$P(S) = \frac{\int \cdots \int \exp[-(1/kT)\bar{V}_{\mathrm{c}}(\bar{b};X) - \gamma\,\mathrm{tr}(XK_{\mathrm{c}}X')]\mathrm{d}X/\mathrm{d}S}{\int \cdots \int \exp[-(1/kT)\bar{V}_{\mathrm{u}}(\bar{b};X) - \gamma\,\mathrm{tr}(XK_{\mathrm{u}}X')]\mathrm{d}X/\mathrm{d}S} \quad (10)$$

It has been emphasized in the formulation of network distribution theory that the difference between the effects of nonbonded interactions on the cross-linked polymer and the un-cross-linked polymer must not be ignored. The implication is that an integration over coordinates that would remove the explicit dependence of eq 10 on the nonbonded potential must not be executed too early. If one does so, eq 10 degenerates to a phantom network model and only a C_1 Mooney–Rivlin term can be obtained. In addition, upon solving for $S°$, the network is found to collapse in the unstrained state.

The nonbonded interactions are treated within the approximation provided by a density fluctuation treatment. The nonbonded potential is replaced by an integral of the Helmholtz free energy density, $a[\rho(\mathbf{r})]$, where the density $\rho(\mathbf{r})$ is an implicit function of the coordinates X through the standard equation

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - X_j) \quad (11)$$

with X_j being the coordinates of segment j. The free energy is expanded as a function of the density fluctuations about the mean density $\bar{\rho}$, which gives

$$\bar{V}(\bar{b};X) \approx a(\bar{\rho})V - \frac{1}{2}a''(\bar{\rho})\bar{\rho}^2 + \frac{1}{2}a''(\bar{\rho}) \int [\rho(\mathbf{r})]^2\,\mathrm{d}\mathbf{r} \quad (12)$$

where V is the volume of the system. Substitution of eq 12 into eq 10 results in

$$P(\mathbf{S}) = \frac{\int \exp[-(a''/kT) \int [\rho_{\mathrm{c}}(\mathbf{r})]^2\,\mathrm{d}\mathbf{r} - \gamma\,\mathrm{tr}(XK_{\mathrm{c}}X')]\mathrm{d}X/\mathrm{d}S}{\int \exp[-(a''/kT) \int [\rho_{\mathrm{u}}(\mathbf{r})]^2\,\mathrm{d}\mathbf{r} - \gamma\,\mathrm{tr}(XK_{\mathrm{u}}X')]\mathrm{d}X/\mathrm{d}S} \quad (13)$$

Upon performing a Fourier expansion of the density (eq 11) and evaluating the terms of the expansion as functions of the components of the gyration tensor, eq 13 yields the elastic equation of state as

$$A_{\mathrm{el}} = D_1(S_1 + S_2 + S_3) + D_2[(1/S_1 + 1/S_2 + 1/S_3) - b'(1/S_1^{\,2} + 1/S_2^{\,2} + 1/S_3^{\,2})] \quad (14)$$

where

$$D_1 = 3\nu kT\kappa_1/2\langle r^2\rangle_0 \quad (15a)$$

and

$$D_2 = \frac{cV_2^{\,2}|S|^{-1/2}}{\beta\phi_2^{\,2} + V_1\phi_1/kT(1 - \phi_1\chi')} \quad (15b)$$

Here V_1 is the molar volume of the solvent, $V_2 = N\bar{V}_2$ is the volume of the elastomer evaluated at the mean density, ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively, and b' and c are the two free parameters of the theory. The compressibility coefficient of the system is β. For the swollen network it is assumed that

$$\beta = \phi_1\beta_1 + \phi_2\beta_2 \quad (16)$$

The interaction parameter, χ, for the system is assumed to be a function of the composition, and the derivative with volume fraction is $\chi' = 2\chi_0 + 3\chi_1\phi_2 + ...$, as appears in eq 15b.

Analysis of Swelling

For isotropic swelling, $S_1 = S_2 = S_3$, and $\lambda = \lambda_1 = \lambda_2 = \lambda_3$. In the unstrained state, $\lambda = 1$, and it follows from eq 14 that

$$A_{\mathrm{el}}{}^{\circ} = 3D_1S_1{}^{\circ} + 3D_2{}^{\circ}(1/S_1{}^{\circ} - b'/(S_1{}^{\circ})^2) \qquad (17)$$

where the superscript denotes the unstrained state, and

$$D_2{}^{\circ} = cV_2{}^2/\beta_2(S_1{}^{\circ})^{3/2} \qquad (18)$$

is obtained from eq 15b on setting $\phi_1 = 0$ as appropriate for the unstrained, i.e., unswollen, state. We may further eliminate one of the variable parameters by making use of the condition that the unstrained state should minimize the free energy of the elastic body. For the isometric distortions of interest, this condition reads

$$\partial A_{\mathrm{el}}{}^{\circ}/\partial S_1{}^{\circ} = 3D_1 - 3D_2{}^{\circ}\left(\frac{5}{2}\frac{1}{(S_1{}^{\circ})} - \frac{7}{2}\frac{b'}{(S_1{}^{\circ})^3}\right) = 0 \qquad (19)$$

It follows that

$$D_2{}^{\circ} = D_1(S_1{}^{\circ})^2/\left(\frac{5}{2} - \frac{7}{2}b\right) \qquad (20)$$

where $b = b'/S_1{}^{\circ}$. Upon applying eq 20 to eq 15b, D_2 is reduced to the form

$$D_2 = \frac{D_2{}^{\circ}}{F(\phi_2)} = \frac{D_1(S_1{}^{\circ})^2}{\left(\frac{5}{2} - \frac{7}{2}b\right)F(\phi_2)} \qquad (21)$$

where

$$F = F(\phi_2) = \beta_2{}^{-1}\left(\beta\phi_2 + \frac{V_1}{kT}\frac{\phi_1}{\phi_2(1 - \phi_1\chi')}\right) \qquad (22)$$

Upon inserting eq 21 into eq 14 and using the condition of isotropic swelling, the elastic free energy can be expressed as

$$A_{\mathrm{el}} = 3D_1S_1{}^{\circ}\left[\lambda^2 + \frac{2}{(5 - 7b)F}\left(\frac{1}{\lambda^2} - \frac{b}{\lambda^4}\right)\right] \qquad (23)$$

The dilation modulus is defined as

$$G^{\mathrm{d}} = \frac{1}{3RT\lambda V_0}\left(\frac{\partial A_{\mathrm{el}}}{\partial\lambda}\right)_{P,T} \qquad (24)$$

and when the required differentiation is carried out on eq 23, the result is

$$G^{\mathrm{d}} = C_1\left\{1 + \frac{1}{(5 - 7\mathrm{b})F}\left[\left(-\frac{2}{\lambda^4} + \frac{4b}{\lambda^6}\right) - \frac{1}{F}\left(\frac{1}{\lambda^3} - \frac{b}{\lambda^5}\right)\frac{\partial F}{\partial\lambda}\right]\right\} \qquad (25)$$

where

$$C_1 = 2D_1S_1{}^{\circ}/RTV_0 = \frac{3\nu\kappa_1S_1{}^{\circ}}{\langle r^2\rangle_0} \qquad (26)$$

and

$$\left(\frac{\partial F}{\partial\lambda}\right) = -\frac{3}{\beta_2\lambda^4}\left[\beta_1 + 2(\beta_2 - \beta_1)\phi_2 + \frac{V_1}{kT}\frac{\chi'\phi_1{}^2 + 3\chi_1\phi_1{}^2\phi_2 - 1}{\phi_2{}^2(1 - \phi_1\chi')^2}\right] \qquad (27)$$

The combination of eqs 25–27 enables one to calculate the dilation modulus, given the interaction parameter for the polymer–solvent pair together with the required equation of state data.

Table I
Thermodynamic Parameters for Polymer and Solvents at 30 °C

substance	$\beta \times 10^3$ (cm^3/J)	V_1 (cm^3/mol)	V_1/RT (cm^3/J)
PDMS[25]	1.232		
benzene[26,27]	1.027	89.94	3.568×10^{-2}
n-heptane[26,27]	1.527	148.4	5.888×10^{-2}
DMP[27-29]	1.54	146.0	5.793×10^{-2}
TMP[28,30]	1.64	167.1	6.630×10^{-2}
cyclohexane[31]	1.189	109.4	4.340×10^{-2}
cyclohexane[28,a]	1.066	108.1	4.435×10^{-2}

[a] Data at 20 °C.

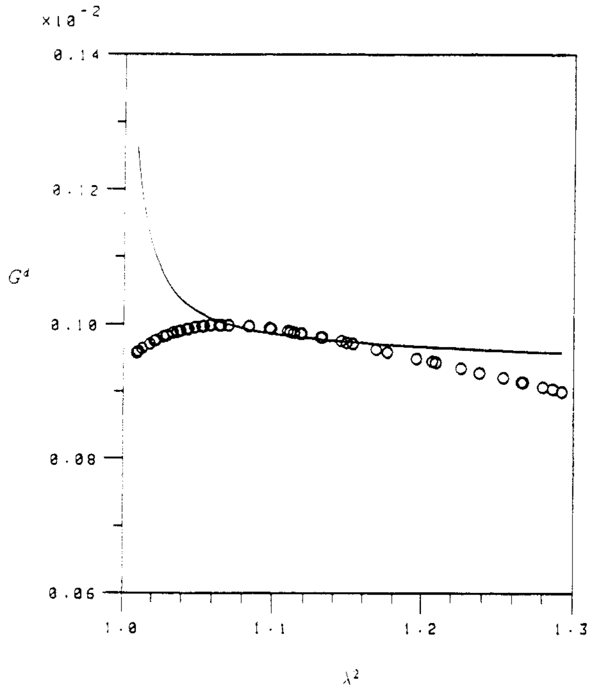

Figure 1. Comparison of experimental results for the dilation modulus G^{d} and the predictions of network distribution theory for PDMS + *n*-heptane. Circles represent experimental results, and the solid curve is the theoretical prediction with $b = 0.970$ and $C_1 = 9.40 \times 10^{-4}$.

Results and Discussion

The thermodynamic constants for the systems reported in paper 1 that are needed for the theoretical calculations are tabulated in Table I. The dilation moduli calculated according to eqs 24–26 were fitted to those obtained from the experiments by adjusting the values of C_1 and b in eq 25. Values of the coefficients of the polynomial expressions for the χ functions are reported in paper 1. In Figure 1 we have plotted the theoretically predicted dilation modulus for the poly(dimethylsiloxane) (PDMS) + *n*-heptane system at 30 °C (solid curve) together with the experimental results, represented by the circles, as functions of the square of the extension ratio for the system. Similarly, Figures 2–4 are the corresponding plots for the systems PDMS + 2,3-dimethylpentane (DMP), PDMS + 2,2,4-trimethylpentane (TMP), and PDMS + benzene, respectively. The values of C_1 and b used to obtain the given theoretical curves are tabulated in Table II.

Further comparisons of theory with data can be made. Neuburger's data[10] on PDMS with cyclohexane has been analyzed also, and plots of the theoretical and measured dilation moduli, G^{d}, against λ^2 are shown in Figures 5–8 for two different PDMS networks (one was cross-linked

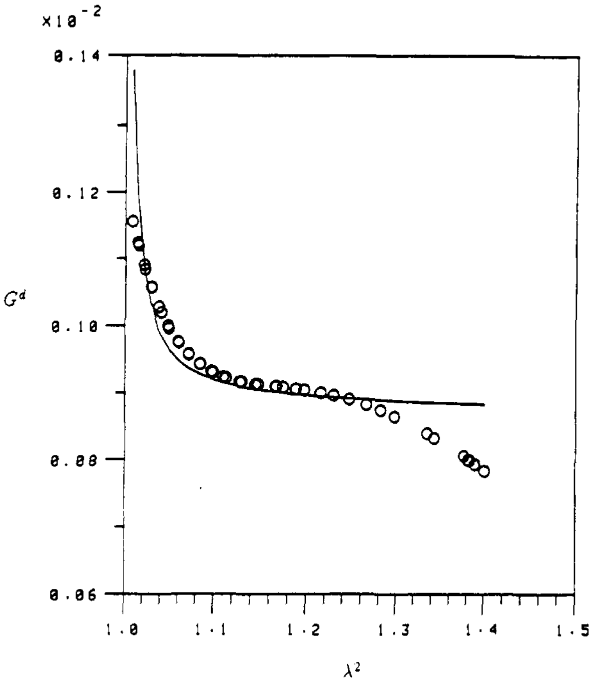

Figure 2. Comparison of experimental results and theory for PDMS + 2,3-dimethylpentane. Circles represent experimental results, and the solid curve represents the prediction with $b = 0.970$ and $C_1 = 8.70 \times 10^{-4}$.

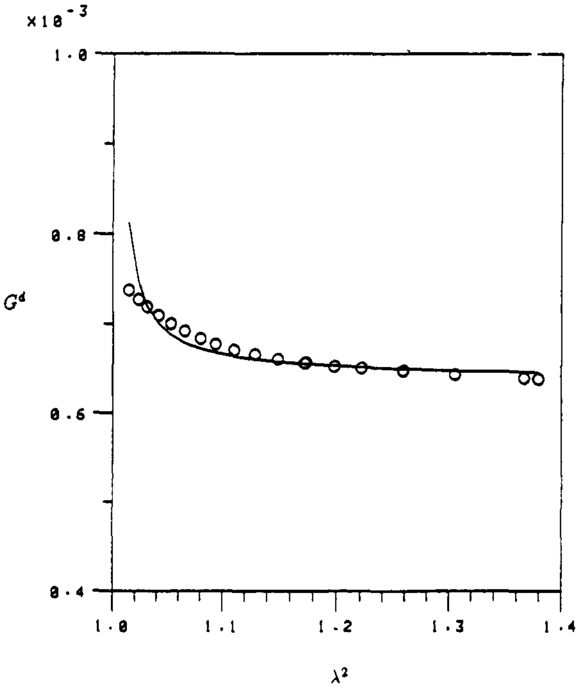

Figure 3. Comparison of experimental results and theory for PDMS + 2,2,4-trimethylpentane. Circles represent experimental results, and the solid curve is the theoretical result calculated with $b = 0.976$ and $C_1 = 6.38 \times 10^{-4}$.

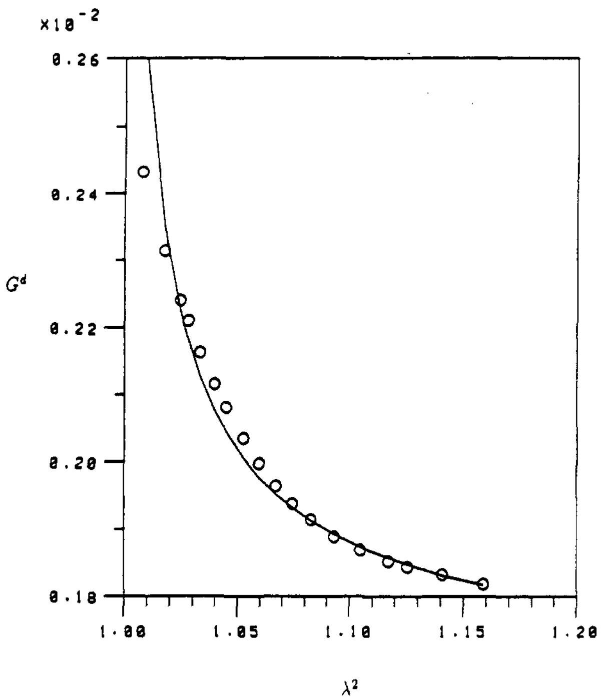

Figure 4. Comparison of experimental results and theory for PDMS + benzene. Circles represent experimental results, and the solid curve is calculated from theory with $b = 0.960$ and $C_1 = 1.69 \times 10^{-3}$.

Table II
Values of b and C_1 for PDMS with Different Solvents

system	b	C_1	system	b	C_1
benzene	0.960	1.69×10^{-3}	DMP	0.970	8.70×10^{-4}
heptane	0.970	9.40×10^{-4}	TMP	0.976	6.38×10^{-4}

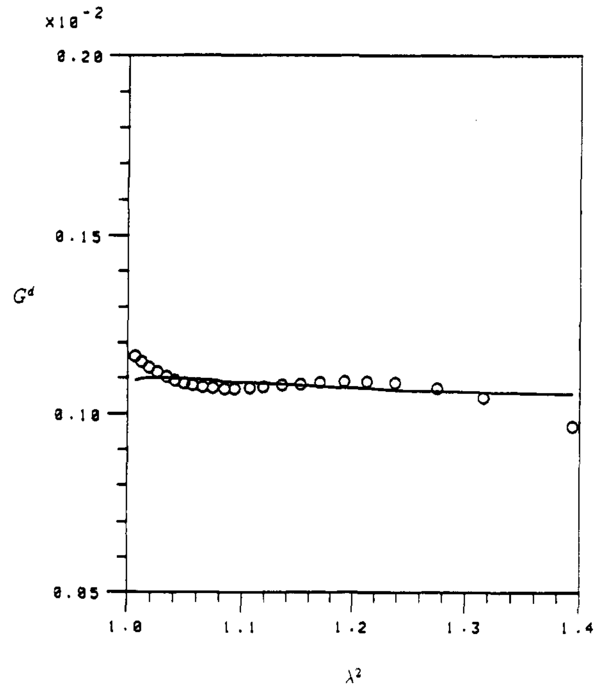

Figure 5. Dilation modulus G^d vs λ^2 for cyclic PDMS + cyclohexane at 20 °C calculated with $b = 0.982$ and $C_1 = 1.04 \times 10^{-3}$.

with 1,3,5,7-tetramethylcyclotetrasiloxane, referred to as cyclic PDMS in the captions; the other was cross-linked with tetraethoxysilane, referred as Si(OEt)$_4$ PDMS) at different temperatures. Circles again signify experimental results, and solid curves are the theoretical predictions. The values of C_1 and b used are given in Table III. As the temperature increases, C_1 has to be greatly decreased while b stays almost constant.

As shown in the graphs, the theoretical predictions fit very well with the experimental results for the selected values of C_1 and b. However, closer inspection reveals that the agreement is achieved at the expense of unphysical variation in the values of the parameters. First, as indicated previously,[19] a reasonable range for b is $0 < b < {}^5/_{11}$. The b values listed in Tables II and III are clearly outside this range. Second, C_1 and b are parameters that should depend upon the polymer only; they should be the same for all the solvent systems with the same polymer

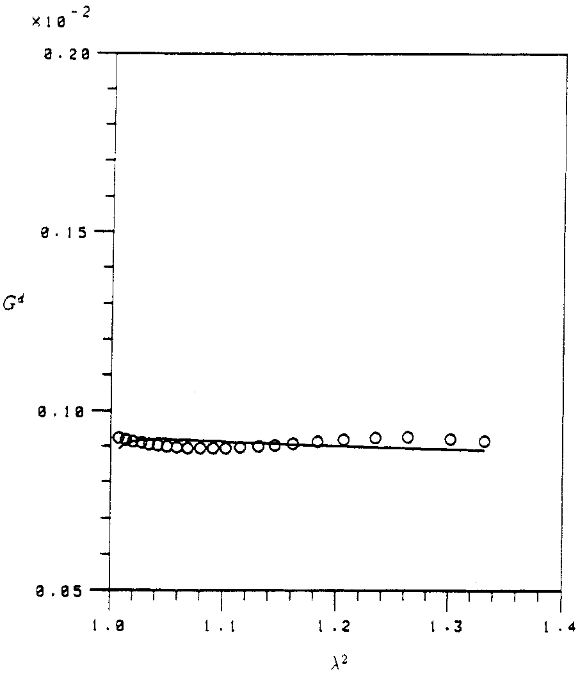

Figure 6. Dilation modulus G^d vs λ^2 for cyclic PDMS + cyclohexane at 30 °C calculated with $b = 0.982$ and $C_1 = 8.71 \times 10^{-3}$.

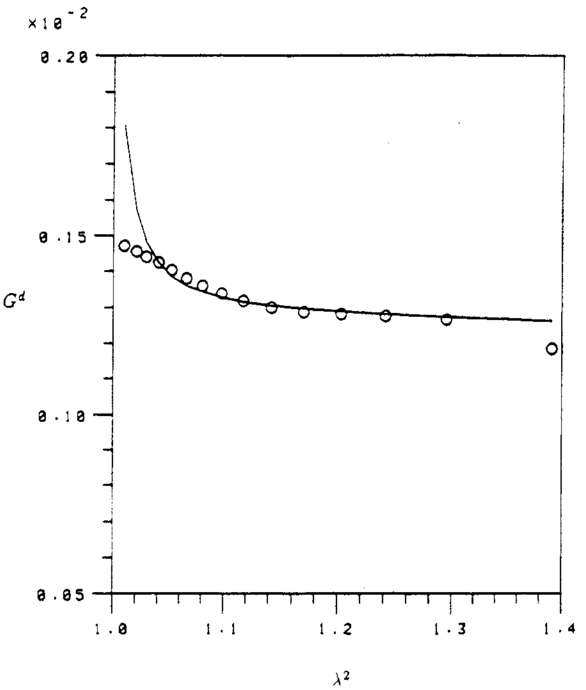

Figure 7. Dilation modulus G^d vs λ^2 for Si(OEt)$_4$ PDMS + cyclohexane at 20 °C with $b = 0.968$ and $C_1 = 1.24 \times 10^{-3}$.

network, but they are not. The values of b average to 0.972 ± 0.0066 (standard deviation), which is not a great variation. More troublesome is the much larger variation in C_1. The values in Table II average to $(1.03 \pm 0.46) \times 10^{-3}$, while those in Table III for the cyclic PDMS average to $(0.96 \pm 0.12) \times 10^{-3}$, and for Si(OEt)$_4$ PDMS the average plus standard deviation of C_1 is $(1.13 \pm 0.15) \times 10^{-3}$. The reason for treating the averages for b and C_1 differently is that b should be a universal parameter, whereas C_1 depends upon the network structure. If we ignore the latter point and simply take the average and standard deviation for all the C_1 data in Tables II and III, we obtain $C_1 = (1.04 \pm 0.10) \times 10^{-3}$.

The predicted dilation modulus functions, G^d, obtained with the average values $b = 0.969$ and $C_1 = 1.03 \times 10^{-3}$ for the four different solvent systems are displayed in Figure 9, along with the experimental results. The squares represent the experimental measured dilation moduli[3,24] for PDMS + benzene, circles for PDMS + n-heptane, crosses for PDMS + 2,3-dimethylpentane, and triangles for PDMS + 2,2,4-trimethylpentane. The long-dashed curve is the predicted dilation modulus for PDMS + benzene, the short-dashed curve is for PDMS + n-heptane,

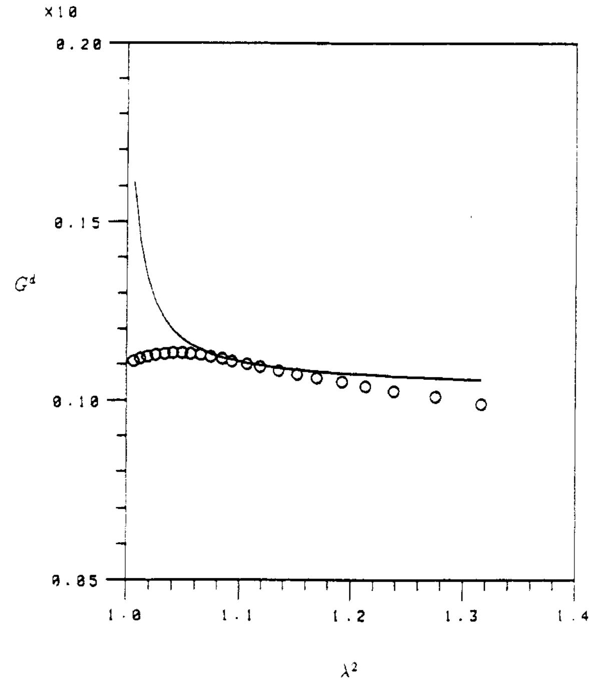

Figure 8. Dilation modulus G^d vs λ^2 for Si(OEt)$_4$ PDMS + cyclohexane at 30 °C with $b = 0.966$ and $C_1 = 1.03 \times 10^{-3}$.

Table III
Values of b and C_1 for PDMS with Cyclohexane

cross-linker	t (°C)	b	C_1
cyclic	20	0.982	1.04×10^{-3}
cyclic	30	0.982	8.71×10^{-4}
Si(OEt)$_4$	20	0.968	1.24×10^{-3}
Si(OEt)$_4$	30	0.966	1.03×10^{-3}

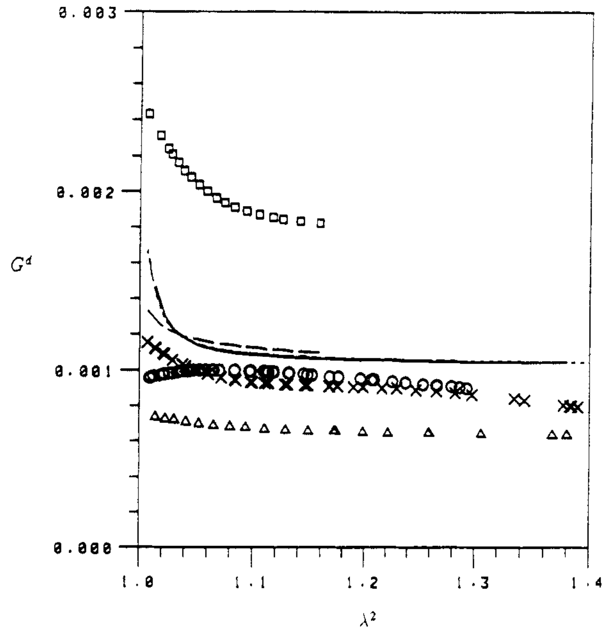

Figure 9. Comparisons between experimental results and theoretical predictions for different solvent systems. (See text for a detailed explanation of the symbols.)

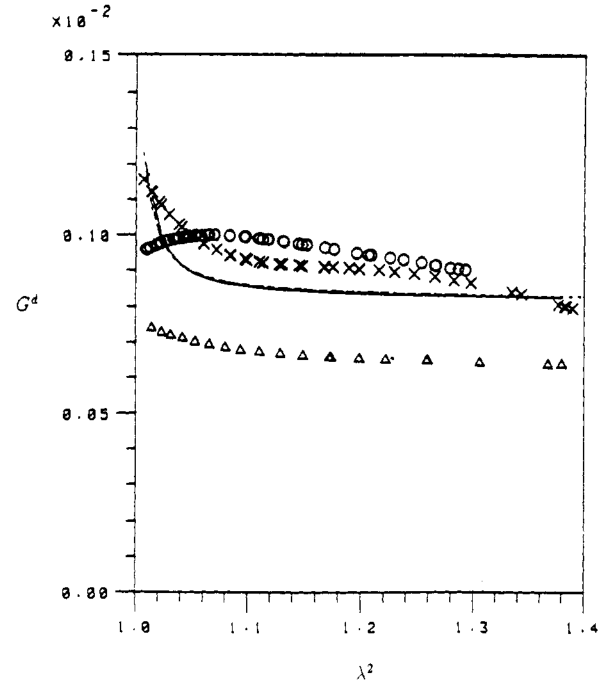

Figure 10. Theoretical predictions with $b = 0.969$ and $C_1 = 1.03 \times 10^{-3}$ along with the experimental results for three of the systems. The solid curve is for PDMS + TMP, the dotted is for PDMS + TMP, and the dashed is for PDMS + *n*-heptane. The symbols for the experimental results have the same meanings as in the previous graphs.

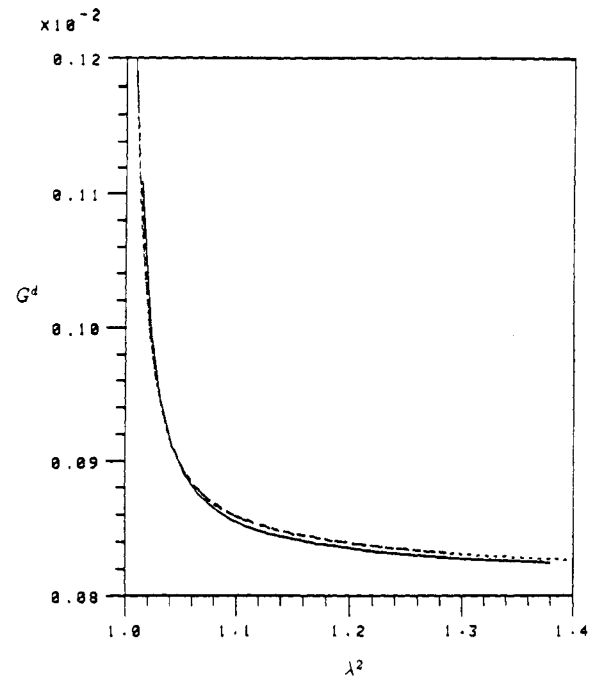

Figure 11. Enlarged presentation of the theoretical predictions shown in Figure 10.

the dotted curve (scarcely visible) is for PDMS + 2,3-dimethylpentane, and the solid curve is for PDMS + 2,2,4-trimethylpentane. Although the experimental results and the predicted values are no longer in good agreement with use of averaged parameters, at least the theory successfully predicts the general trends in the data. Theory predicts that the dilation moduli increase with increasing χ, and that is indeed the experimental result. However, it is easily inferred by inspection of Figures 1–9 that the theoretical predictions are extremely sensitive to the values of the parameters C_1 and b—so much so that this sensitivity largely masks that due to variations in the χ parameters. We will have more to say about this later.

To emphasize the χ dependence of the theoretical dilation modulus, we have plotted the values of G^d for the alkane diluents only in Figure 10. In this case, the average values of the parameters, $C_1 = 8.16 \times 10^{-4}$ and $b = 0.972$, pertinent for these three systems alone have been used. Also shown in this figure are the experimental results. The predicted values are shown again in Figure 11 at a magnified scale. In this case the experimental results have been omitted, but the identification of the curves is the same as in the previous graphs.

Conclusions

The discrepancies between the variable values of the parameters required to fit the data and the constancy of the same as required by the theory are most likely due to inaccuracies in the functional form of the D_2 term. One of us pointed out that this function is not adequate to explain results in the biaxial stretch region;[19] the function of λ multiplying the D_2 coefficient varies much too rapidly with λ. In the theoretical work, this term arose from a series expansion of the density fluctuations. The expansion was worked out to the two terms that have been used here (see eq 14). This problem, of the functional form of the D_2 term, influences the coefficient D_1 by changing it from a perfectly determinable structural coefficient to a variable dependent on the parameter that enters into the function of the deformation that multiplies the coefficient D_2. This happens at the stage of minimizing the free energy to determine the unstrained state, and at this point the C_1 coefficient becomes dependent upon b. But then, to fit the data, b goes out of bounds, and this in turn renders the functional form suspect.

Efforts have been made to search for other, more suitably scaled F functions (see eq 21) and for different renditions of the function multiplying D_2. The exponent of the term in the determinant, $|S|$, in eq 15b has been replaced by a variable, and the consequences of choosing values of the exponent within the range of −2 to +3 were investigated. As the exponent increases, the derivative of F with respect to ϕ_2 decreases. Values of the exponent in the vicinity of unity appear to be most promising, but it happens that there is then no reasonable value for b that yields a positive value for the Mooney–Rivlin "constant" C_2. Further efforts to explore the functional form of the D_2 term of eq 14 have also been attempted. A few functions having the same, at least to the first term, series expansion as

$$\left(\frac{1}{S_1}+\frac{1}{S_2}+\frac{1}{S_3}\right)-b'\left(\frac{1}{S_1^{\,2}}+\frac{1}{S_2^{\,2}}+\frac{1}{S_3^{\,2}}\right)$$

have also been tried, but the results are no better.

Notwithstanding these quantitative and rigorous tests and the not altogether satisfactory results therefrom, it must be noted that the general features of the theory seem to account extremely well for the dilation data taken one diluent at a time. It is further noted that the total variation of the parameters, about ±10% for C_1 and less than ±1% for b, is an exceptionally small variation vis-à-vis the established norms of traditional theories of elasticity. We believe that the theory contains the essentials of an advance in understanding elastomers, including their swelling behavior, but that further work is required to improve the quantitative aspects of the functional form of the density fluctuation term.

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