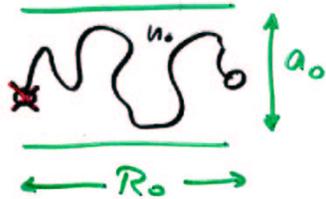


Entangled Rubber Networks

① Entanglement:



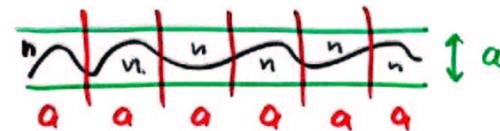
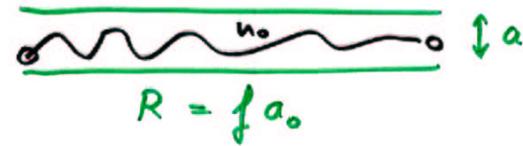
$$\frac{W}{3kT} = \frac{1}{2} \frac{R_0^2}{n_0 b^2} + \frac{1}{2} \frac{n b^2}{a_0^2}$$

$$\frac{\partial W}{\partial n_0} = 0 \Rightarrow \frac{n_0}{R_0} = \frac{a_0}{b^2}$$

$$\frac{W}{3kT} = \frac{n_0 b^2}{a_0^2} \stackrel{!}{=} 1 \Rightarrow \begin{aligned} a_0^2 &= n_0 b^2 \\ R_0 &= a_0 \end{aligned}$$

$$\boxed{W = 3kT \nu_0}$$

② Deformation



$$\frac{W_s}{3kT} = \frac{n b^2}{a^2} = 1$$

$$M = \frac{n_0}{n} = \frac{a_0^2}{a^2} = f^2$$

$$\boxed{W = 3kT \nu_0 M} \quad (1)$$

③ Stress Tensor : affine Rotation

$$\underline{\underline{\sigma}} - p \underline{\underline{E}} = 3kT \nu_0 M \underline{\underline{S}} \quad (2)$$

$$\underline{\underline{S}} = \left\langle \frac{\underline{u}' \underline{u}'}{u'^2} \right\rangle$$

$$\underline{u}' = \underline{F}^{-1} \cdot \underline{u}$$

$$u' = |\underline{F}^{-1} \cdot \underline{u}|$$

④ Virtual Work

$$\frac{\partial W}{\partial t} = \underline{\underline{\sigma}} : \underline{\underline{D}} \underline{\underline{u}}$$

$$\Rightarrow \frac{\partial M}{\partial t} = M \underline{\underline{S}} : \underline{\underline{D}} \underline{\underline{u}} \Rightarrow M = e^{\langle \ln u' \rangle}$$

⑤ "Small" Deformations ($\lambda_u \leq 100\%$):

$$e^{\langle \ln u' \rangle} \approx e^{\langle u' \rangle - 1} \approx \langle u' \rangle + \frac{1}{2} (\langle u' \rangle - 1)^2 + \dots$$

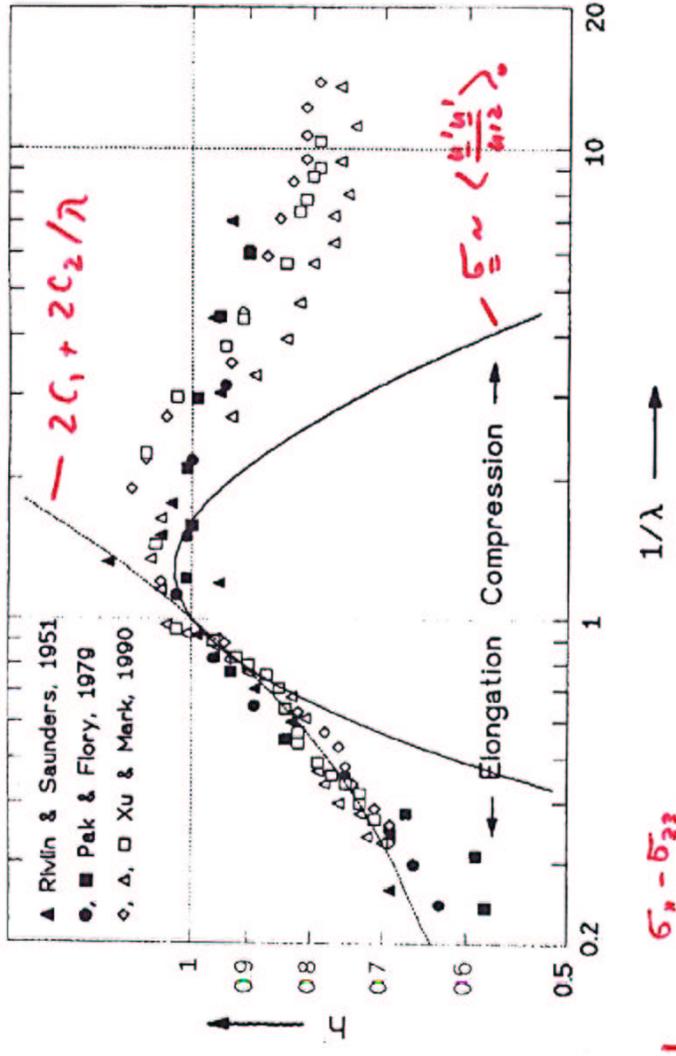
For $G_{\infty} \leq G_{N \text{ melt}}$:

$$\underline{\underline{\sigma}} - p \underline{\underline{E}} = G_{\infty} \left[\langle u' \rangle + \frac{1}{2} (\langle u' \rangle - 1)^2 \right] \underline{\underline{S}}$$

⑥ For $G_{\infty} \geq G_{N \text{ melt}}$:

$$\underline{\underline{\sigma}} - p \underline{\underline{E}} = G_N \left[\langle u' \rangle + \frac{1}{2} (\langle u' \rangle - 1)^2 \right] \underline{\underline{S}} + 3G_c \langle \underline{u}' \underline{u}' \rangle$$

with $G_{\infty} = G_N + G_c$



$$h = \frac{\sigma_x - \sigma_{z3}}{G_w(\lambda^2 - 1/\lambda)}$$

FIG. 1. Normalized Mooney stress $h = \sigma_M/G_w$ of several crosslinked rubbers (symbols) as a function of inverse extension ratio $1/\lambda$. Broken line is given by the normalized Mooney-Rivlin equation (13). Line represents Doi-Edwards damping function in elongation, Eq. (15), and compression, Eq. (16).

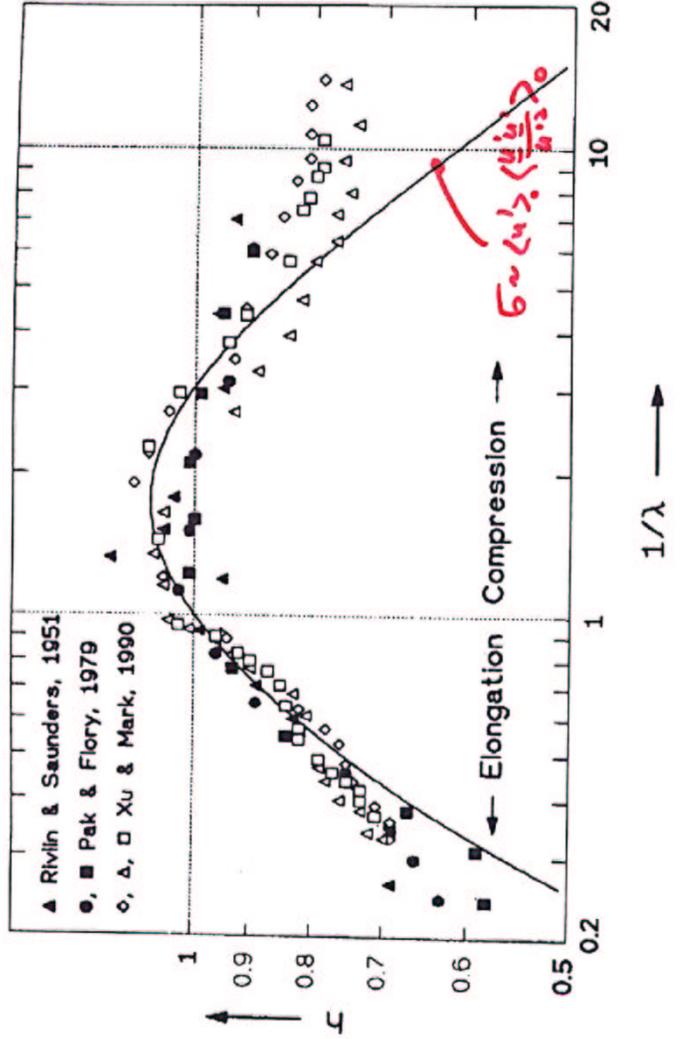


FIG. 6. Normalized Mooney stress $h = \sigma_M/G_w$ of several rubbers (symbols) as a function of inverse extension ratio $1/\lambda$. Curve is the prediction by the linear molecular stress theory, in elongation, Eq. (20), and compression, Eq. (21). From Wagner (1993), reproduced with permission of Hüthig and Wepf Verlag, Basel.

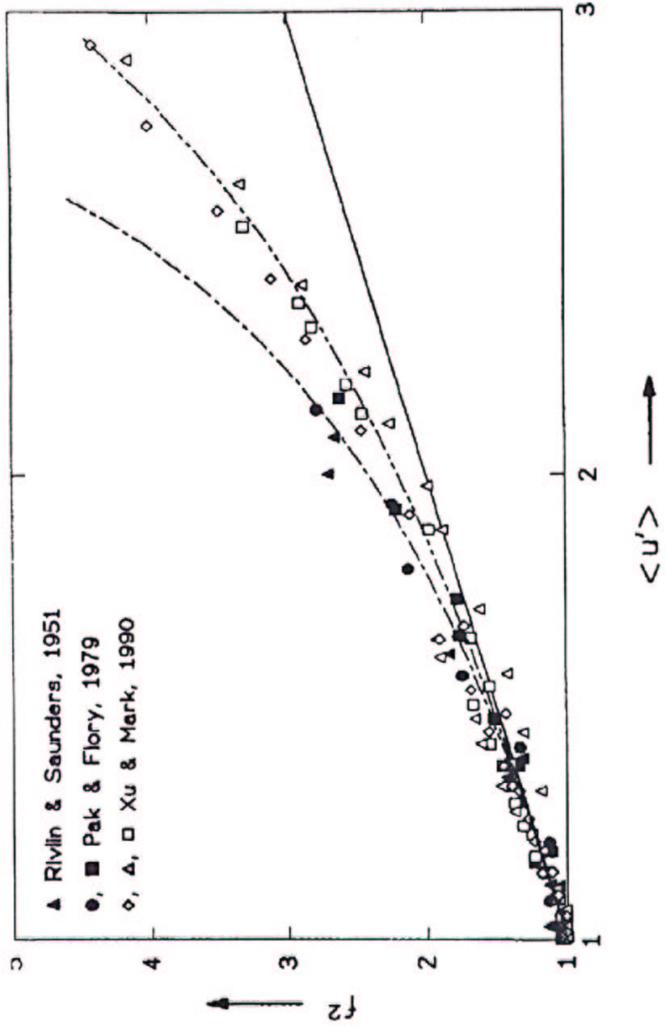
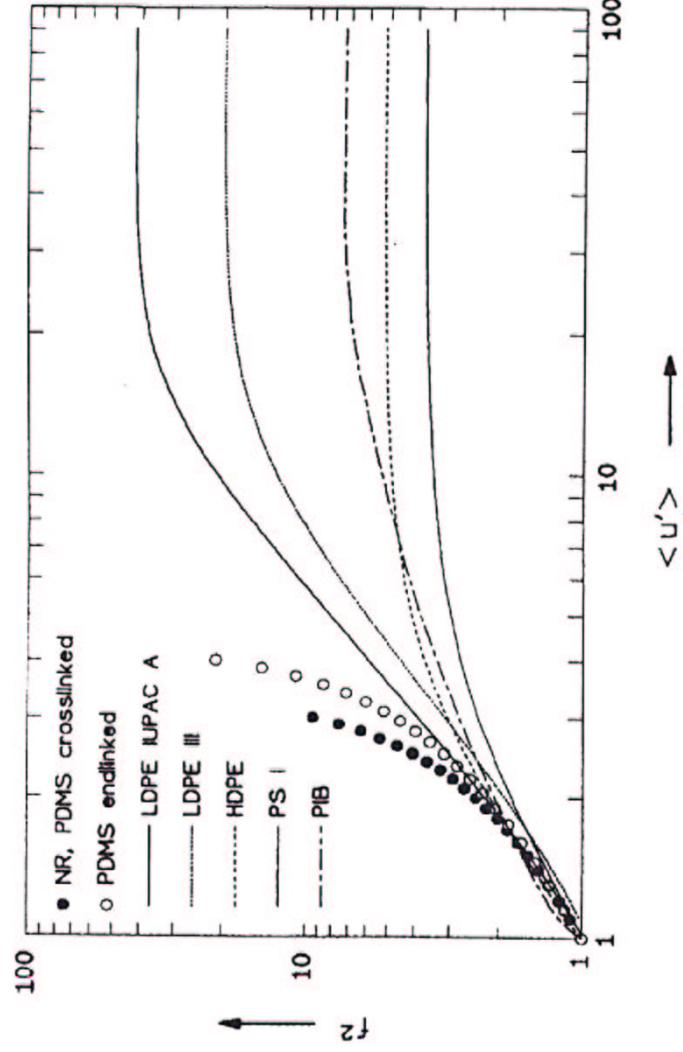


FIG. 7. Square of molecular stress function f^2 as a function of average stretch $\langle u' \rangle$ for elongation and compression of several rubbers. Solid line represents $f^2 = \langle u' \rangle$, broken lines are given by Eq. (22) with $\langle u' \rangle_{\max} = 3.4$ for randomly crosslinked networks and $\langle u' \rangle_{\max} = 4.3$ for end-linked networks. From Wagner (1993), reproduced with permission of Hüthig and Wepf Verlag, Basel.



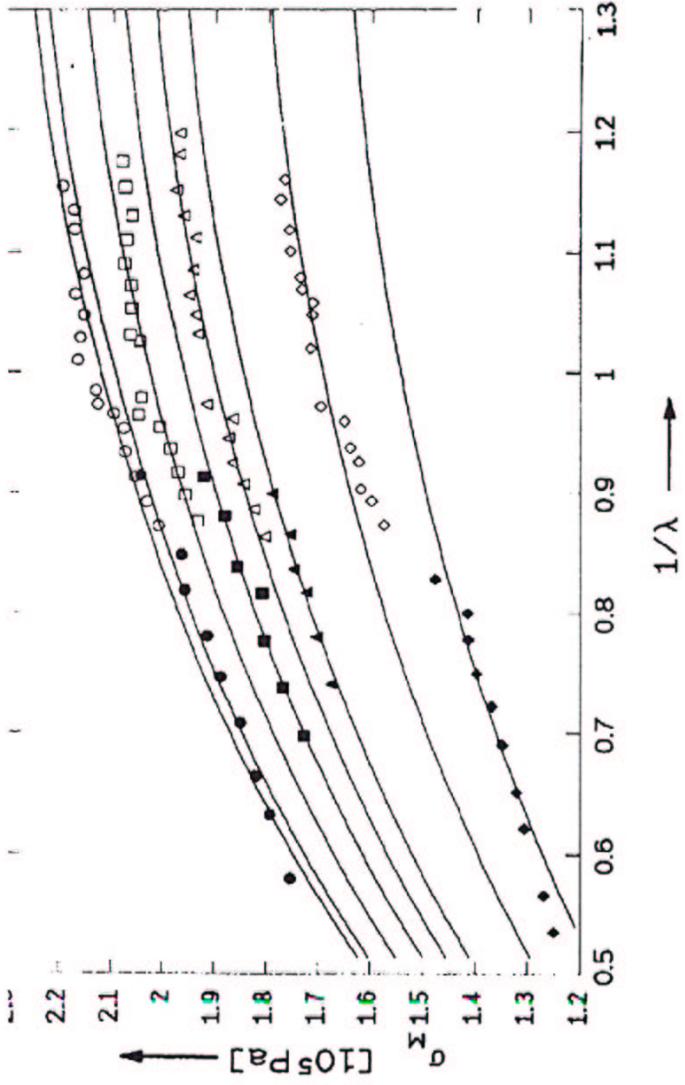


FIG. 8. Mooney stress σ_M of radiation crosslinked PDMS networks (data from Erman and Flory, 1978b). Lines are predictions of the linear molecular stress theory, Eq. (19).

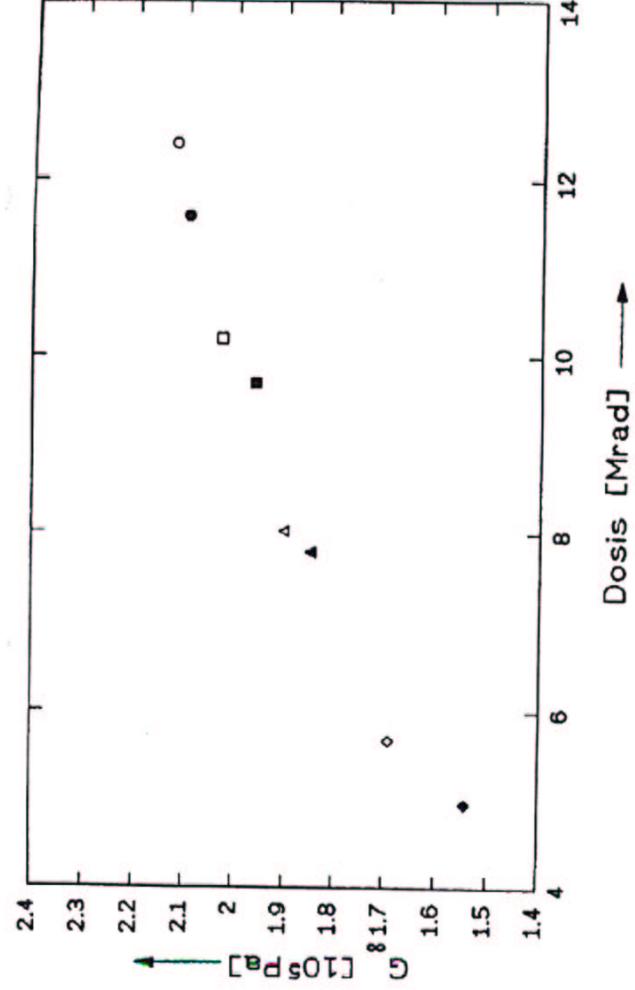
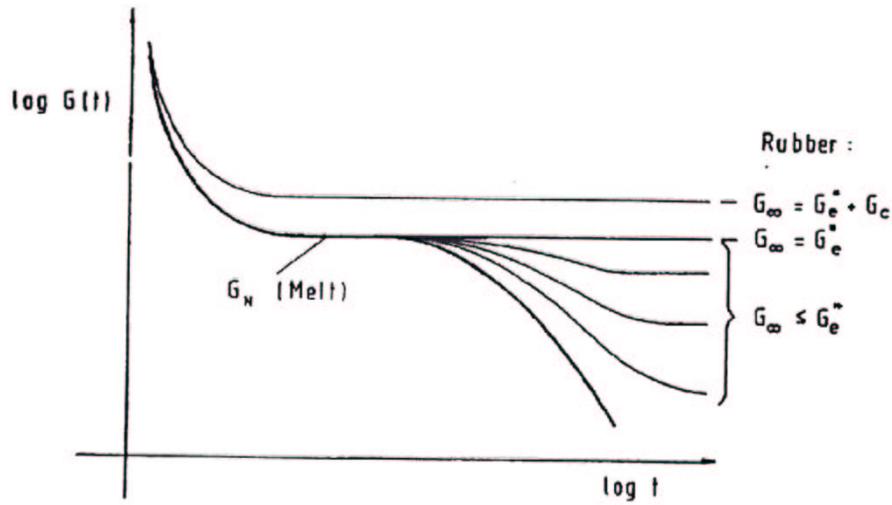
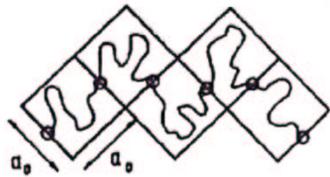


FIG. 9. Small-strain equilibrium shear modulus G_∞ from Fig. 12 as a function of radiation dosage.



a) Melt : $G_M = \frac{3}{5} k T c \frac{b^2}{a_e^2}$



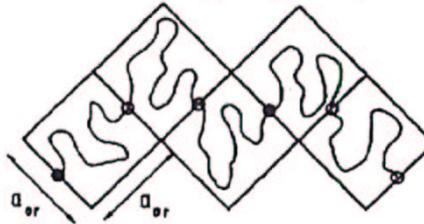
⊖ Entanglement

c) Rubber : $G_\infty = G_e^* = G_M$



● Crosslink

b) Rubber : $G_\infty < G_e^* = G_M$



d) Rubber : $G_\infty > G_e^* = G_M$



FIG. 3. The transition from melt to rubber: The tube (for details see the text).

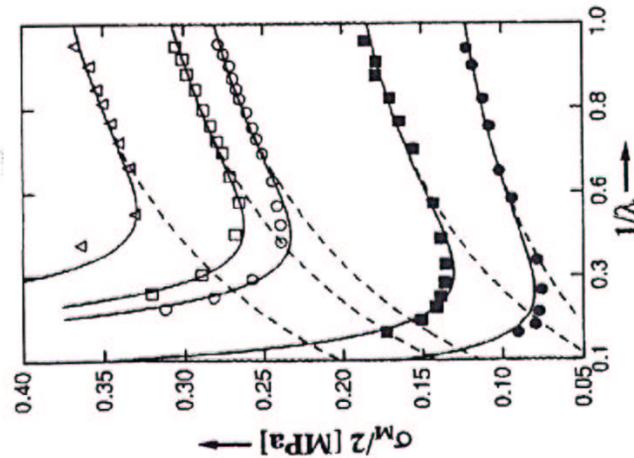
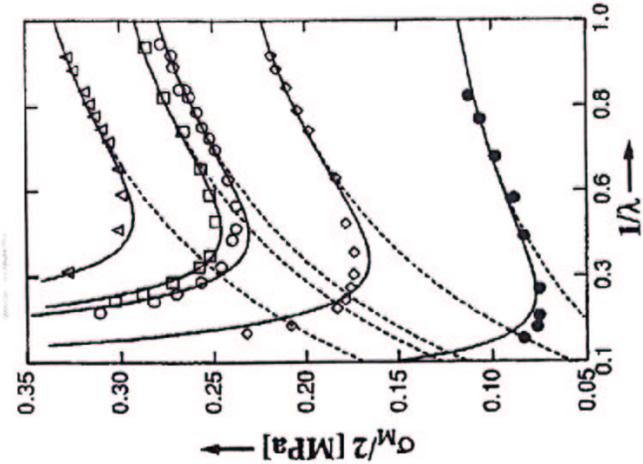


FIG. 4. Mooney stress $\sigma_M/2$ for rubber networks B1 (bottom)-B5 (top), left, and rubber networks C1 (bottom)-C5 (top), right. Data (symbols) from Mullins (1959b). Full symbols represent networks with $G_\infty < G_e^*$, open symbols networks with $G_\infty > G_e^*$. Fit by Eq. (29) (lines). Broken lines are predictions for $S = 1$.

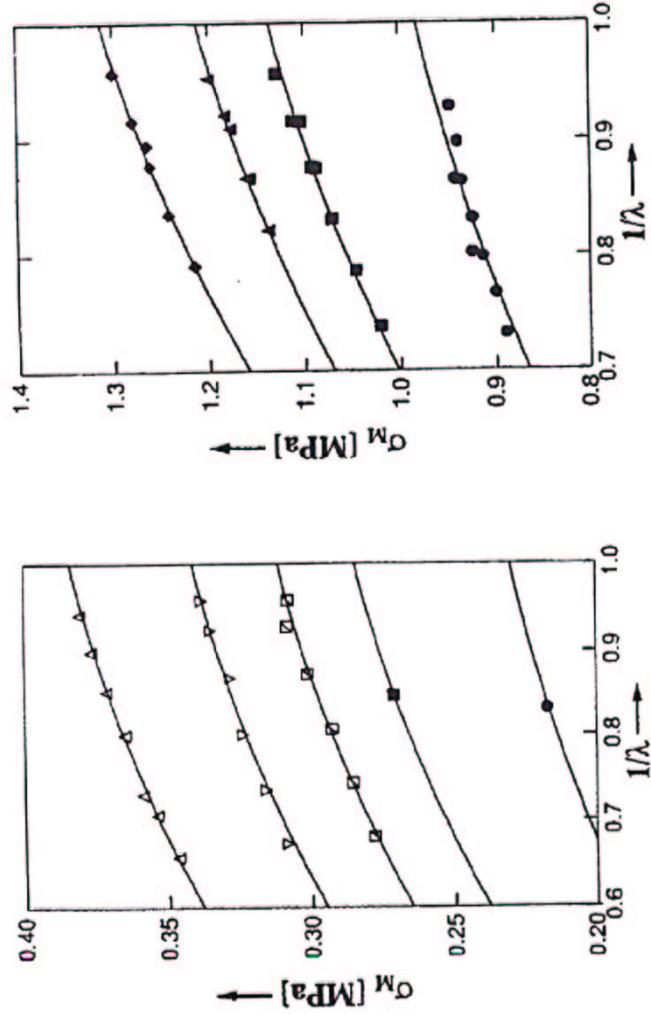
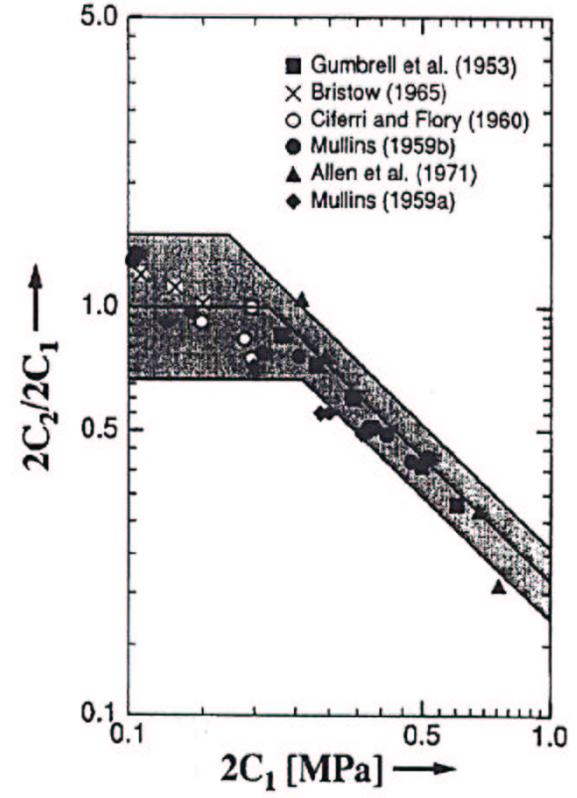


FIG. 6. Mooney stress σ_M for radiation cured polybutadiene networks. Data (symbols) from Dossin and Graessley (1979). Full symbols represent networks with $G_\infty < G_e^*$, open symbols networks with $G_\infty > G_e^*$. Lines are fits by Eq. (29) with $S = 1$. Left: Networks crosslinked in bulk from sample Pb344. Right: Networks crosslinked and measured at polymer volume fraction $v = 0.50$ from sample PB168S.



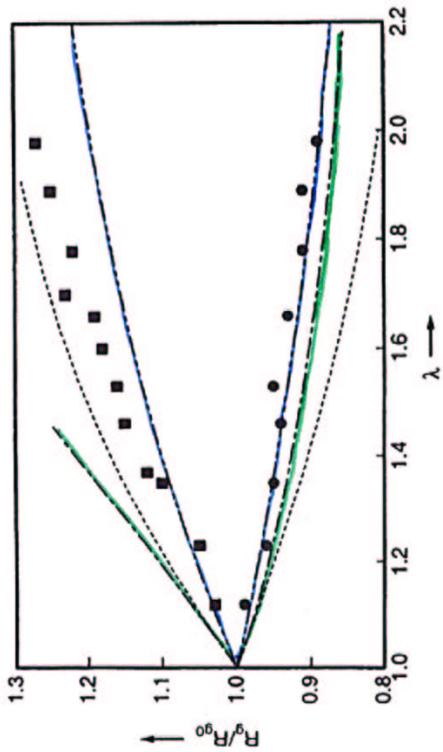


Figure 1. Relative radius of gyration R_g/R_{g0} for labeled elementary chains as a function of elongational stretch λ [(■) parallel and (●) perpendicular to the direction of stretch] from Beltzung et al.⁴ on PDMS rubber cross-linked in bulk with $M_n = 10000$. Curves are predictions of the following models: (—) junction affine, eqs 7 and 8; (---) affine rotation, approximation of Boué et al.,³ eqs 12 and 13; (-.-.-) affine rotation, exact result, eqs 18 and 19.

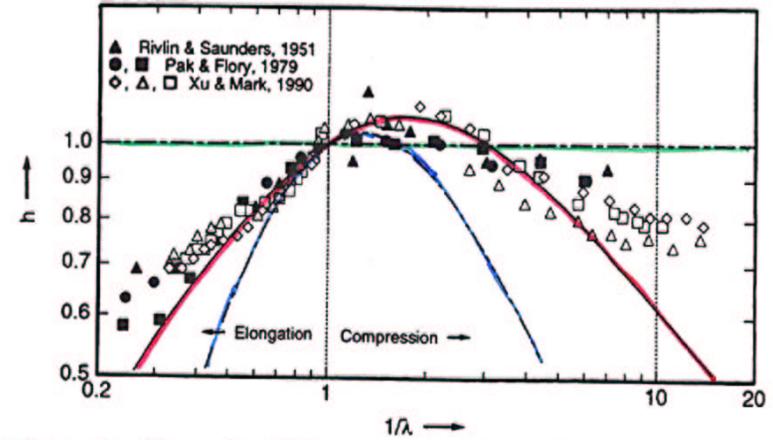


Figure 3. Normalized Mooney stress h as a function of inverse elongational stretch ratio $1/\lambda$. Data (symbols) are for several rubber networks. Curves are predictions of the following models: (—) junction affine, eq 27; (---) affine rotation, eq 28; (-.-.-) linear molecular stress function theory, eq 29.

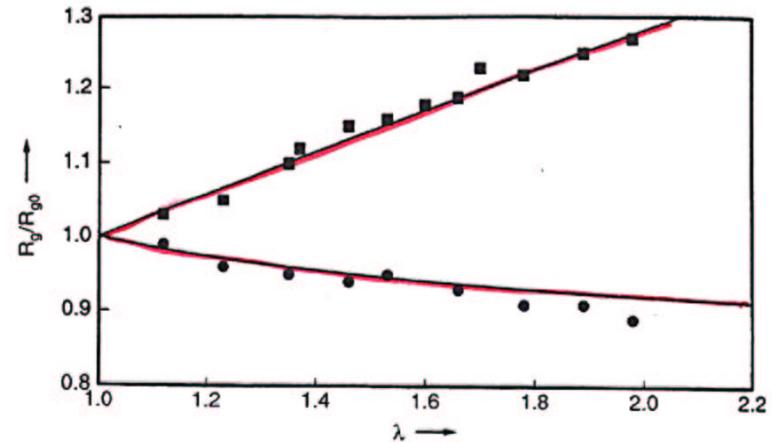


Figure 2. Relative radius of gyration R_g/R_{g0} for labeled elementary chains as a function of elongation stretch λ [(■) parallel and (●) perpendicular to the direction of stretch] from Beltzung et al.⁴ on PDMS rubber cross-linked in bulk with $M_n = 10000$. Curves are predictions of the linear molecular stress function theory, eq 24.

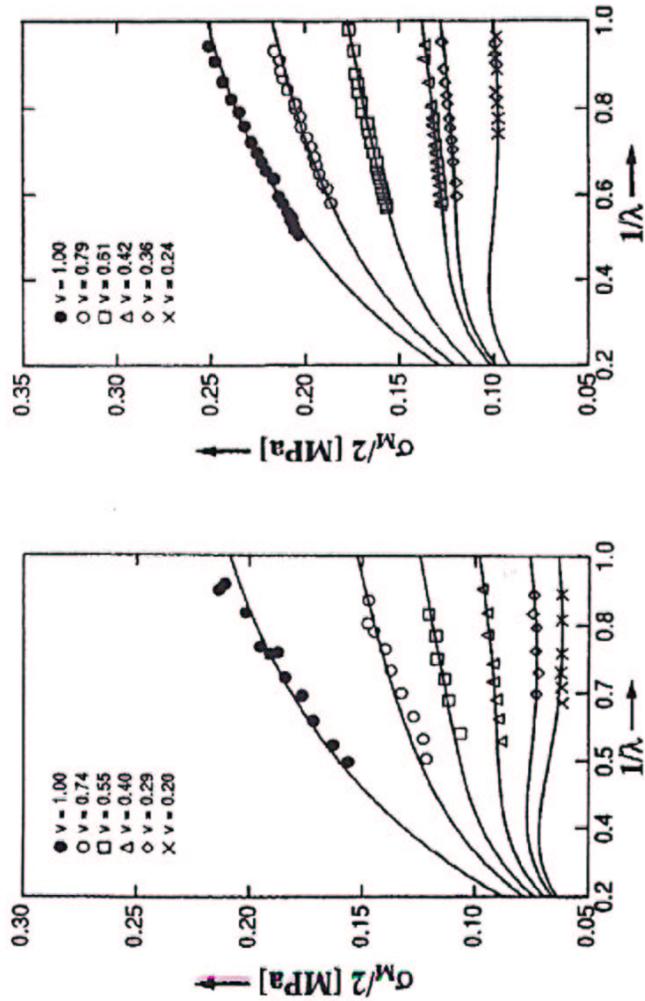


FIG. 9. Mooney stress $\sigma_M/2$ for natural rubber swollen to polymer volume fraction, v . Left: Data (symbols) from Gumbrell *et al.* (1953). Solvent: benzene. Fit by Eq. (64) (lines) with $S_e = 1$. Right: Data (symbols) from Allen *et al.* (1971). Solvent: *n*-decane. Fit by Eq. (65) (lines) with $S_e = S_c = 1$.

$$\bar{\sigma} - p \bar{\epsilon} = G_v \left[1 + \frac{G_{\infty}}{G_v} (\langle u^2 \rangle_0 - 1) \right] S_e^2, \quad G_v = v^{3/2} G_{\infty}$$

Summary

- ① For $G_{\infty} \leq G_{N_{melt}}$, there is no distinction between the phantom network (crosslinks) and the entanglement network.
- ② There is a phantom network contribution for $G_{\infty} > G_{N_{melt}}$.
- ③ For $G_{\infty} \leq G_{N_{melt}}$, one (1) material parameter (G_{∞}) is sufficient to characterize the stress-strain relations of rubber in bulk as well as swollen in θ -solvent.