Elasticity Theory. III. Volume Exclusion and C_2[1]

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ABSTRACT: The interaction between density fluctuations and strain in an elastomer is analyzed in an approximate way. A term behaving like the C_2 term of the Mooney–Rivlin theory is obtained. The coefficient C_2 depends upon the interaction parameter characterizing the polymer–solvent mixture; in the absence of solvent, C_2 depends upon the compressibility of the polymer.

Recent experiments[2] to determine stress–strain isotherms of elastomers have shown conclusively that the Mooney–Rivlin[3] equation

$$\Delta A_{\text{el}} = C_1(\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2 - 3) + C_2(\lambda_1{}^{-2} + \lambda_2{}^{-2} + \lambda_3{}^{-2} - 3) \quad (1)$$

is required to explain results. Here ΔA_{el} is the (Helmholtz) elastic free energy, C_1 and C_2 are constants dependent on temperature, degree of swelling, number of cross-links, etc., and $\lambda_1, \lambda_2, \lambda_3$ are principle extension ratios.

If one considers a uniform expansion of the elastomer, *i.e.*, $\lambda_1, \lambda_2, \lambda_3 \rightarrow \infty$, it will be noted by inspection of eq 1 that the C_1 term contributes an increasingly large contribution to the free energy, while the C_2 term decreases algebraically. It is well known from the molecular theory[4] that the C_1 term is due to the attractive force between cross-links. Therefore, C_2 is due, at least in part, to repulsions. We will show, on the basis of a simplified analysis, that a term behaving like the C_2 term can be obtained from consideration of the interaction of density fluctuations with the strain. The derivation is admittedly crude in that free energies are equated with potentials of mean force and no account is taken of the network structure. Yet the result seems to describe, at least qualitatively, the solvent dependence of C_2, and possibly the temperature dependence as well.

We begin by assuming that the attractive and repulsive parts of the potential of mean force acting between a pair of cross-links directly connected by a chain are separable. The attractive force is a result of the entropic restoring force delivered by the connective chain, and additionally by those chains connecting the pair of cross-links in question by circuitous paths.[5] The repulsive potential arises because of the excluded-volume interaction between spatial (not topological) neighbors. Close spatial neighboring chains are not necessarily close topological neighbors, and so it seems reasonable to separate the two contributions to the potential. (To be sure, there is a coupling between the repulsive and attractive potentials, especially considering chains on alternate paths between the two cross-links. One can be quite certain that such coupling will be a second or higher order effect.)

The repulsive part of the potential of mean force for the collection of chains in the cross-linked state $a'\{\mathbf{R}\}$ depends upon the positions $\{\mathbf{R}\}$ of centers of gravity of all chains. We want the contribution to the *elastic* free energy, and so must subtract from this the potential $a\{\mathbf{R}\}$ for the same system without cross-links. Following Fixman[6] in spirit as well as notation, this difference between potentials of mean force may be written as

$$a'\{\mathbf{R}\} - a\{\mathbf{R}\} = \frac{1}{2} V_2{}^2\epsilon^{(2)}\sum_{i,j}\int [W_i'(\mathbf{r})W_j'(\mathbf{r}) - W_i(\mathbf{r})W_j(\mathbf{r})]\mathrm{d}\mathbf{r} \quad (2)$$

where V_2 is the molecular volume of a polymer segment, the sum is over all pairs of chains i and j (including self-interaction), $W_i'(\mathbf{r})$ is the segment density at $\mathbf{r}$ from chain i located at $\mathbf{R}_i$ in the cross-linked state, and $W_i(\mathbf{r})$ is the corresponding quantity in the un-cross-linked state. In eq 2 the term $\epsilon^{(2)}$ is related to the Flory–Huggins expression

$$\epsilon = (kT/V_1)[\phi_1 \ln \phi_1 + \chi\phi_1\phi_2]$$
$$\epsilon^{(2)} = \mathrm{d}^2\epsilon/\mathrm{d}\phi_2{}^2 = (kT/V_1)[\phi_1{}^{-1} - 2\chi] \quad (3)$$

in which kT has its usual meaning, V_1 is the molecular volume of solvent, $\phi_1 = 1 - \phi_2$ is the volume fraction of solvent, and χ is the interaction parameter. We have assumed χ to be concentration independent; that is not correct in general,[7] but the elaboration to account for concentration dependence is easy and of no concern here. Comments on the divergence of this expression will follow.

Introduction of cross-links in the polymer reduces the effective segment density per chain. Consider a pair of chains in close proximity: in one configuration let there be a cross-link between a pair of arbitrary segments, one from each chain; in the other configuration there is no cross-link. With centers of gravity of the molecules fixed, as they would be in a real network, it is obvious that the configuration space available to the cross-linked pair of chains is smaller, because of the constraint, than the configuration space available to the un-cross-linked chains. It seems to be difficult to develop the theory along these lines in a quantitative way. We reserve these considerations for a future time.

Nevertheless, we are able to get a qualitative description of the system. The segment density $\eta(\mathbf{r})$ at a point $\mathbf{r}$ in space is given by

$$\eta(\mathbf{r}) = \sum\delta(\mathbf{r} - \mathbf{r}_j) = \sum{}'\delta(\mathbf{r} - \mathbf{r}_j) + \sum{}''\delta(\mathbf{r} - \mathbf{r}_j)$$

where the sum is over all segments j located at $\mathbf{r}_j$. The sum may be separated into two terms; the first is over all segments that are not cross-links, while the second is over cross-links. The density $\eta(\mathbf{r})$ applies equally well to the whole system and

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(2) (a) G. Allen, M. J. Kirkham, J. Padget, and C. Price, *Trans. Faraday Soc.*, **67**, 1278 (1971); (b) R. M. Johnson and J. E. Mark, *Macromolecules*, **5**, 41 (1972).

(3) A recent review has been published by K. Dušek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969).

(4) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XI.

(5) B. E. Eichinger, *Macromolecules*, **5**, 496 (1972).

(6) M. Fixman, *J. Chem. Phys.*, **35**, 889 (1961).

(7) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).

to a single chain. In either case the number of segments must be conserved, and so a cross-link should be thought of as a pair of segments that forever occupy the same point in space.

Now average $\eta(\mathbf{r})$ over all positions of segments subject to fixed centers of gravity of the molecules and cross-links. Then, for a molecule in the cross-linked state

$$W_c(\mathbf{r}) = \langle\eta(\mathbf{r})\rangle = \langle\sum{}'\delta(\mathbf{r} - \mathbf{r}_j)\rangle + \sum{}''\delta(\mathbf{r} - \mathbf{r}_j) = W'(\mathbf{r}) + \sum{}''\delta(\mathbf{r}-\mathbf{r}_j)$$

If cross-links are *absent* one has

$$W_u(\mathbf{r}) = n(\gamma/\pi)^{3/2} \exp(-\gamma\boldsymbol{\varrho}^2) \tag{4}$$

where γ is a parameter inversely proportional to the unperturbed dimension of the chain (all chains are assumed to have the same number of segments n) and $\boldsymbol{\varrho}$ is the vector from the center of gravity of chain i to $\mathbf{r}$; the center of gravity of chain i is $\mathbf{R}_i$. We will assume that $W'(\mathbf{r})$ is likewise Gaussian, but with the n in eq 4 replaced by n'. Since segments must be conserved, $n' < n$. The cross-links are introduced in an equilibrium state, and it is therefore reasonable to assume that $W_c(\mathbf{r}) = W_u(\mathbf{r}) = W(\mathbf{r})$. Thus, for chain i

$$W_i'(\mathbf{r}) = W_i(\mathbf{r}) - \delta W_i(\mathbf{r}) \tag{5}$$

with

$$\delta W_i(\mathbf{r}) = \delta n(\gamma/\pi)^{3/2} \exp(-\gamma\boldsymbol{\varrho}^2)$$

With use of eq 5 the integrand in eq 2 may be expanded, with retention of linear terms only, to

$$W_i'(\mathbf{r})W_j'(\mathbf{r}) - W_i(\mathbf{r})W_j(\mathbf{r}) = -[W_i(\mathbf{r})\delta W_j(\mathbf{r}) + W_j(\mathbf{r})\delta W_i(\mathbf{r})]$$

and eq 2 becomes

$$a'\{\mathbf{R}\} - a\{\mathbf{R}\} = -V_2^2\epsilon^{(2)}\sum_{i,j}\int W_i(\mathbf{r})\delta W_j(\mathbf{r})\mathrm{d}\mathbf{r} \tag{6}$$

One may ignore the interaction between segments and cross-links, because the cross-links are very dilute.

If Fixman's theory[6] is followed at this stage, we rapidly run into impossible integrals. What is required is to integrate the exponential function of eq 6 with the radial distribution function,w hich involves $\exp[X\exp(-a\mathbf{R}^2)]$. Instead, we interpret eq 6 as the elastic free energy, and integrate the set of positions $\{\mathbf{R}\}$ over the volume V of the elastomer. Furthermore, the double sum may be collapsed to one integration with respect to the radial distribution function, assumed to be equal to unity in both strained and unstrained states, and the other sum is then trivial. Thus, we obtain

$$\Delta A_{\mathrm{el}}' = -(\nu^2V_2^2/V)\epsilon^{(2)}(n\delta n)(\gamma/\pi)^3\int\mathrm{d}\mathbf{R}\int\exp[-\gamma(\mathbf{r} + \mathbf{R})^2] \exp[-\gamma\mathbf{r}^2]\mathrm{d}\mathbf{r} \tag{7}$$

where $\Delta A_{\mathrm{el}}'$ is the contribution to ΔA_{el} from repulsions.

Strain

As the elastomer is deformed, so are the chains. It is usually assumed that the deformation is affine, so that every point $\mathbf{r}$ in space is sent to $\mathbf{r}'$ by the transformation

$$\mathbf{r}' = \boldsymbol{\lambda}\mathbf{r} \tag{8}$$

where the deformation gradient tensor $\boldsymbol{\lambda}$ has components

$$\lambda_{\alpha\beta} = \partial x_\alpha'/\partial x_\beta$$

With respect to the molecular theory above, the deformation acts on δW_i, but not on W_i. This is a crucial point which we need to justify. Equation 6 is a convolution of the distribution function in the un-cross-linked state with (an approximate representation of) the distribution function which describes the effect of the cross-links. If we attempt to deform both $W_i(\mathbf{r})$ and $\delta W_i(\mathbf{r})$ we get nothing. What this means is that chains in the un-cross-linked state will not sustain a deformation at equilibrium. Thus, we obtain

$$\delta W_i(\mathbf{r}) = (\delta n)|\boldsymbol{\lambda}|^{-1}(\gamma/\pi)^{3/2} \exp[-\gamma\tilde{\boldsymbol{\varrho}}(\boldsymbol{\lambda}\tilde{\boldsymbol{\lambda}})^{-1}\boldsymbol{\varrho}] \tag{9}$$

where now the coordinates represent the strained state. (The primes have been left off for clarity.) Use of eq 9, 6, and the analysis leading to eq 8 yields

$$\Delta A_{\mathrm{el}}' = -(\nu^2V_2^2/V)\epsilon^{(2)}(n\delta n)(\gamma/\pi)^3\int\mathrm{d}\mathbf{R}\int \exp[-\gamma(\mathbf{r} + \mathbf{R})^2] \exp[-\gamma\mathbf{r}^2]\{1 - \gamma\tilde{\mathbf{r}}\mathbf{S}\mathbf{r} + \ldots\}\mathrm{d}\mathbf{r} \tag{10}$$

where

$$S = (\boldsymbol{\lambda}\tilde{\boldsymbol{\lambda}})^{-1} - \mathbf{E} \tag{11}$$

Equation 10 has been obtained by assuming $\mathbf{S}$ small, so that the exponential in which it occurs may be expanded and only the linear term retained. The integrals in eq 10 are readily performed to yield

$$\Delta A_{\mathrm{el}}' = (\nu^2V_2^2/2V)\epsilon^{(2)}(n\delta n)[\mathrm{Tr}(\mathbf{S}) - 2] \tag{12}$$

where

$$\mathrm{Tr}(\mathbf{S}) = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3$$

Thus

$$\begin{aligned} C_2 &= (\nu^2V_2^2/2V)\epsilon^{(2)}n\delta n \\ &= kT(V/V_1)\phi_2^2(1/2\phi_1 - \chi)(1 - n'/n) \end{aligned} \tag{13}$$

It will be noted that $\epsilon^{(2)}$, see eq 3, is divergent as $\phi_1 \rightarrow 0$. Fixman has noted[6] that in this limit the use of an average potential between molecules is inappropriate and segmental interactions must be considered. Since the time of Fixman's work, Helfand and Tagami[8] have shown that in the absence of solvent $\epsilon^{(2)}$ should be replaced by a term which depends upon the compressibility of the polymer. As the volume fraction of polymer approaches unity, C_2 will become inversely proportional to the compressibility and hence will be finite.

The major features of C_2 found experimentally[2a] are in accord with eq 13. In particular, $C_2 = 0$ when $\phi_1 = 1/2\chi$; experiments of Allen, *et al.*,[2a] show C_2 to vanish near $\phi_1 \cong 0.8$, so that $\chi \cong 0.62$, a reasonable value to expect for natural rubber-*n*-decane. Furthermore, C_2 from eq 13 increases with increasing polymer concentration and reaches a finite limit as $\phi_2 \rightarrow 1$. In the absence of any statement about the magnitude of $(1 - n'/n)$, or more particularly its temperature dependence, one concludes that $\mathrm{d}C_2/\mathrm{d}T \propto \kappa$, the enthalpy of dilution parameter;[7] and so the temperature coefficient of C_2 contains a positive contribution for those solvents that mix endothermally with the polymer. There are exceptions to endothermal mixing, *e.g.*, polyisobutylene–pentane. Perhaps measurements on such a system would yield negative values for $\mathrm{d}C_2/\mathrm{d}T$.

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