Macromolecules **1995,** *28,* 4303–4306

Soft Rubber Elasticity

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Received November 21, 1994; Revised Manuscript Received February 10, 1995⊗

ABSTRACT: Nematic elastomers, because of their internal orientational degree of freedom, have been predicted to possess some totally soft modes of distortion. Their free energy is predicted not to rise when certain strains λ are imposed. We give explicit examples of such strains and then investigate whether these stress-free strains, more typical of liquids, remain soft when the network chains have compositional fluctuations. We conclude that random copolymer nematic elastomeric networks are hardened very slightly to give moduli along the previously soft directions between 10^{-8} and 10^{-4} times that of the equivalent nonnematic rubber.

I. Introduction

The resistance to deformation in conventional elastomers is largely entropic. The number of conformations accessible to a chain diminishes when its end points are separated. When entropy drops, the free energy rises and an external applied stress is required to impose such a deformation. By contrast a nematic network, where chains are spontaneously anisotropic before any stress is applied, can theoretically[1] respond by changing chain shape (at an entropy cost) and by rotating and distorting the now anisotropic distribution of chains. The latter, by itself, does not cost entropy and hence no free energy. Certain deformations λ avoid chain shape change and merely rotate the distribution of chains. We have termed these "soft"[1] since the free energy does not rise and therefore no stress is required. The deformations are liquidlike in effect.

In section II we briefly introduce nematic elastomers and then analyze the soft λs. They are not small (up to 40% or more), and they are not simple body rotations. They were anticipated on general grounds by Golubovic and Lubensky,[2] who recognized that an internal degree of freedom such as a nematic director in a mobile solid (nonglassy) can have this degeneracy. Olmsted[3] has further considered such modes and their anomalous scattering power.

Experimentally, electric fields rather than the imposition of strain have been used to explore the internal freedom of these unusual solids. Both Zentel[4] and Mitchell *et al.*[5] found that shape change in nematic monodomains could be induced by anomalously low fields. The expected field required (assuming no soft response) can be crudely estimated by comparing electric $(1/2)\epsilon_0\Delta\epsilon E^2$ and elastic μ field energies (where $\mu = 10^5-10^6$ J/m^3 is the shear modulus of the rubber and $\Delta\epsilon$ the dielectric anisotropy). Experimentally, responses were observed at between 10^{-4} and 10^{-2} times lower fields.[4,5] It remains an open question, if the theoretical predications are correct, why any field is needed? Possibilities such as surface anchoring and defects suggest themselves. In concluding we shall look critically at such possibilities.

In section III we shall calculate the effect of compositional fluctuations. If the actual realizations of chains depart from the mean composition, then the rotation mechanism is not able to work completely and a slight hardening results; that is, a small but finite stress or electrical field is required to induce shape change.

II. Nematic Elastomers and "Soft" Elasticity

A nematic Gaussian chain of length L has a mean-square end-to-end size:

$$\langle r_i r_j \rangle = \frac{1}{3} l_{ij} L \tag{1}$$

where the effective step length tensor l_{ij} replaces the single length l of the isotropic case. The relative weight of a chain with its end-to-end vector $\mathbf{r}$ fixed by linkage to the network is

$$P(\mathbf{r}) \propto \exp\left[-\frac{3 r_i l_{ij}^{-1} r_j}{2L}\right] \tag{2}$$

Taking the log gives us the entropy of this strand, and making the usual assumption of affine deformation, we can say that the current strand $\mathbf{r}$ is related to that before deformation, $\mathbf{r}_0$, by $\mathbf{r} = \lambda\cdot\mathbf{r}_0$. We should average the entropy of a given strand over the formation span, $\mathbf{r}_0$, to give the free energy change (per network strand) on distortion λ:

$$\Delta F = kT\frac{3}{2L}\langle \mathbf{r}_0^T\cdot\lambda^T\cdot\mathbf{l}^{-1}\cdot\lambda\cdot\mathbf{r}_0\rangle_{\mathbf{r}_0} \tag{3}$$

$$\Delta F = kT\frac{1}{2}\mathrm{Tr}[\mathbf{l}_0\cdot\lambda^T\cdot\mathbf{l}^{-1}\cdot\lambda] \tag{4}$$

The original shape tensor, defined as in eq 1, $\mathbf{l}_0 = 3\langle\mathbf{r}_0\mathbf{r}_0\rangle/L$ can be different from the current one both in the orientation of its principal axes and in the degree of anisotropy. The length L of the particular strand under consideration (in effect the degree of polymerization) cancels in eq 4 so that polydispersity in strand length does not play a role at this level. We can thus ignore it below.

To simply see that deformations can be at constant free energy, that is, soft, apply

$$\lambda = \mathbf{l}^{1/2}\cdot\mathbf{l}_0^{-1/2} = \mathbf{R}_\theta^T\cdot\mathbf{l}_0^{1/2}\cdot\mathbf{R}_\theta\cdot\mathbf{l}_0^{-1/2} \tag{5}$$

One sees that $F = (1/2)kT\ \mathrm{Tr}[\mathbf{I}] = (3/2)kT$ is equal to the undeformed value. Here $\mathbf{R}_\theta$ is the (unitary) transform tensor for a rotation θ about an axis. The shape tensor $\mathbf{l}$ after deformation can only be a rotated version of the initial $\mathbf{l}_0$ since, if the elastic energy is unchanged,

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⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1995.

0024-9297/95/2228-4303$09.00/0

then the nematic free energy must remain at its minimum, and hence nematic order remains at its initial magnitude and merely suffers a rotation by some angle θ. Since elastomers deform at constant volume, $\det(\lambda) = 1$ is required and eq 5 satisfies this.

The elements $l_\parallel$ and $l_\perp$ specifying the chain shape tensor can be calculated or, better, measured. Neutron scattering gives a direct measure of $l_\parallel$ and $l_\perp$,[6] but it is easier to simply measure[7] the spontaneous distortions of a monodomain elastomer when heated from the nematic state to the isotropic state. Minimization of eq 4 yields the extension on cooling down again, $\lambda_m = (l_\parallel/l_\perp)^{1/3}$, and we use $r^2 = (l_\parallel/l_\perp) = \lambda_{\rm m}^3$ as the fundamental measure of shape anisotropy.

We now specify the concrete form of the soft deformations. Returning to eq 5, we obtain

$$\lambda = \begin{pmatrix} c^2 + s^2/r & cs(r-1) & 0 \\ cs(1-1/r) & c^2 + s^2 r & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{6}$$

where $c = \cos\theta$, $s = \sin\theta$, and there is no distortion along, or shear toward, the rotation axis y. One can deduce from eq 6 that the director rotation θ associated with an imposed λ_{xx} is given by $\sin^2\theta = (\lambda_{xx} - 1)/(\lambda_{\rm m}^{3/2} - 1)$ and that the other components of the soft strain that accompany λ_{xx}, i.e., λ_{zz}, λ_{xz}, and λ_{zx}, are given by $\lambda_{zz} = 1 - (\lambda_{xx} - 1)/\lambda_{\rm m}^{3/2}$, $\lambda_{xz} = [(\lambda_m^{3/2} - \lambda_{xx})(\lambda_{xx} - 1)]^{1/2}$, and $\lambda_{zx} = \lambda_m^{-3/2}[(\lambda_m^{3/2} - \lambda_{xx})(\lambda_{xx} - 1)]^{1/2}$. This deformation has a small rotational component which we can separate out (see Appendix B) leaving a pure shear; however, this complicates the mathematical form of the expression.

An additional arbitrary rotation $\mathbf{R}_\phi$ can be added to eq 5 while retaining the softness of deformations:

$$\lambda = \mathbf{l}^{1/2}\cdot\mathbf{R}_\phi\cdot\mathbf{l}_0^{-1/2} = \mathbf{R}_\theta^T\cdot\mathbf{l}_0^{1/2}\cdot\mathbf{R}_\theta\cdot\mathbf{R}_\phi\cdot\mathbf{l}_0^{-1/2} \tag{7}$$

These rotations do not have to be coaxial with those of the director, that is, with $\mathbf{R}_\theta$, and thus a much larger manifold of soft deformations present themselves.[3] We shall have to return to these additional possibilities below.

The remarkable effect of soft elastic response is a purely nematic-elastomer phenomenon. Residual nematic interactions have long been suspected to be involved in departures from classical behavior in conventional (nonnematic) elastomers. Such forces undoubtedly have an effect on the modulus and also the larger strain behavior of networks, but we are unconcerned by these effects here. The softening to which we refer is, theoretically at least, total.

III. Hardening by Compositional Fluctuations

We now examine how compositional fluctuations can spoil the softness discussed in section II. The uniaxial tensor $\mathbf{l}$ arises from the nematic interactions between monomers on the strand and a nematic field arising from the background of other monomers together with any solvent molecules present and is characterized by its anisotropy, that is, the ratio $a = l_\parallel/l_\perp$. In a mixed system (such as a copolymer) the different types of monomer because of their differing structure will have (at least slightly) different interactions with the nematic field. Furthermore, in random copolymers different chains will randomly have different numbers of each monomer, and so the anisotropy in $\mathbf{l}$, i.e., $l_\parallel/l_\perp$, characterizing the chain will vary from chain to chain. Note that we do not expect a variation in the orientation of $\mathbf{l}$ as this will be set by the nematic field. The free energy per strand will still be given by

$$F = \frac{1}{2}kT\,\mathrm{Tr}[\mathbf{l}_0\cdot\lambda^T\cdot\mathbf{R}_\theta^T\cdot(\mathbf{l}_0)^{-1}\cdot\mathbf{R}_\theta\cdot\lambda] \tag{8}$$

but now that different chains have different $\mathbf{l}$, it is not possible to choose λ and $\mathbf{R}_\theta$ to simultaneously minimize the energy for all chains (except for the trivial case of $\lambda = \mathbf{I}$ and $\theta = 0$, i.e., the starting conditions). The overall free energy is:

$$\overline{\Delta F} = \frac{1}{2}kT\,\overline{\mathrm{Tr}[\mathbf{l}_0\cdot\lambda^T\cdot\mathbf{l}^{-1}\cdot\lambda]} \tag{9}$$

where the $\overline{\cdots}$ indicates averaging over the composition of the strands.

Consider instead a distortion that keeps most of the chains close to their minimum in energy. We choose a general form of λ reminiscent of the soft form in a system with chemically identical chains (in which case $\mathbf{B}$ would simply be $\mathbf{l}_0^{1/2}$):

$$\lambda = \mathbf{R}_\theta^T\cdot\mathbf{B}\cdot\mathbf{R}_\theta\cdot\mathbf{B}^{-1} \tag{10}$$

For the ith strand, initially with $\mathbf{l}_0^i$, the free energy of distortion is:

$$2F/kT = \mathrm{Tr}[\mathbf{B}^{-1}\cdot\mathbf{l}_0^i\cdot\mathbf{B}^{-1}\cdot\mathbf{R}_\theta^T\cdot\mathbf{B}\cdot(\mathbf{l}_0^i)^{-1}\cdot\mathbf{B}\cdot\mathbf{R}_\theta] \tag{11}$$

Because we have $\mathbf{B}$ and $\mathbf{B}^{-1}$, changing the determinant of $\mathbf{B}$ has no effect and eq 11 is governed solely by the characteristic anisotropy $b = b_\parallel/b_\perp$ and becomes:

$$\frac{2F}{kT} = 3 + \left(\frac{\left(\frac{l_\parallel}{l_\perp}\right)}{b^2} + \frac{b^2}{\left(\frac{l_\parallel}{l_\perp}\right)} - 2\right)\sin^2\theta \tag{12}$$

Compositionally averaging $(\overline{\cdots})$ over all chains, we find

$$\frac{2\bar{F}}{kT} = 3 + \left(\frac{\overline{\left(\frac{l_\parallel}{l_\perp}\right)}}{b^2} + b^2\overline{\left(\frac{l_\parallel}{l_\perp}\right)^{-1}} - 2\right)\sin^2\theta \tag{13}$$

To perform the averages in eq 13, we write $l_\parallel/l_\perp = \overline{(l_\parallel/l_\perp)} + \Delta(l_\parallel/l_\perp)$, and assuming deviations $\Delta(l_\parallel/l_\perp)$ from the average are small (as will be justified *post hoc*), we find

$$\frac{2\bar{F}}{kT} = 3 + \left(\frac{\overline{\left(\frac{l_\parallel}{l_\perp}\right)}}{b^2} + \frac{b^2}{\overline{\left(\frac{l_\parallel}{l_\perp}\right)}} - 2\right)\sin^2\theta + \frac{b^2\overline{\left[\Delta\left(\frac{l_\parallel}{l_\perp}\right)\right]^2}}{\left[\overline{\left(\frac{l_\parallel}{l_\perp}\right)}\right]^3}\sin^2\theta \tag{14}$$

Minimizing over b^2, we find $b^2 = \overline{(l_\parallel/l_\perp)}$ plus terms of $O(1/n)$ and the final hardening of the free energy is:

$$\frac{2\bar{F}}{kT} - 3 = \frac{\overline{\left[\Delta\left(\frac{l_{\parallel}}{l_{\perp}}\right)\right]^2}}{\left[\overline{\left(\frac{l_{\parallel}}{l_{\perp}}\right)}\right]^2}\sin^2\theta \qquad (15)$$

We see directly that without compositional variations $\overline{[\Delta(l_{\parallel}/l_{\perp})]^2}$ vanishes and the distortion is totally soft. The anisotropy b of $\mathbf{B}$ returns to that of $\mathbf{l}_0^{1/2}$.

Let us consider a model polymer with n freely jointed rods of type A or B of equal length l but of differing nematic order Q_A and Q_B, reflecting the different interactions the two types of monomer have with the nematic field due to their different structures. The assumption of equal lengths l is for simplicity. An explicit example of $l_A \neq l_B$ is in the appendix. We find in the appendix:

$$\frac{2\bar{F}}{kT} = 3 + \frac{f(1-f)}{n}(Q_A - Q_B)^2\left(\frac{l^2}{3\bar{l}_{\parallel}\bar{l}_{\perp}}\right)^2 \sin^2\theta \qquad (16)$$

Since $f(1 - f) \leq 1/4$, $n = 20{-}200$, and $(Q_A - Q_B)^2 \approx 10^{-2}$, this will generate moduli in the region of 10^{-4}–10^{-8} times those of conventional elastomers. For random copolymers of strand length sufficient to make the response rubbery, the form of eq 16 is quite general, with only the third factor in the coefficient of $\sin^2\theta$ depending weakly on the model adopted, for instance if one allows the two monomer lengths to differ within the freely jointed rod model or if we adopt a worm model of a polymer. In particular, the $f(1 - f)/n$ dependence is the contribution expected from random variations in the composition of each strand (relative numbers of A and B monomers). The tensor $\mathbf{B}$ chosen for the distortion λ is very close to

$$\begin{pmatrix} \bar{l}_{\parallel}^{1/2} & 0 & 0 \\ 0 & \bar{l}_{\perp}^{1/2} & 0 \\ 0 & 0 & \bar{l}_{\perp}^{1/2} \end{pmatrix} = \bar{\mathbf{l}}^{1/2}$$

the value taken in the λ for soft deformations of a network of chemically uniform chains each with a shape tensor identical to the mean shape tensor $\bar{\mathbf{l}}$ in the random copolymer system. The differences between $\mathbf{B}$ and the intuitively obvious choice $\bar{\mathbf{l}}^{1/2}$ generate small terms $O(1/n)$ in the free energy.

One concern remains. Could one make these distortions soft again by employing an $\mathbf{R}_\phi$ in eq 7 different for each strand according to its anisotropy? If we take a reference strand and assign it $\mathbf{R}_\phi = \mathbf{I}$, then for this and the other strand to have the same soft λ and θ, the second strand must have an $\mathbf{R}_\phi$ given by

$$\mathbf{R}_\phi = \mathbf{R}_\theta^T \mathbf{A}^{-1} \mathbf{R}_\theta \mathbf{A} \qquad (17)$$

where $\mathbf{A} = \mathbf{l}_1^{1/2} \cdot \mathbf{l}_0^{-1/2}$, with $\mathbf{l}_1$ and $\mathbf{l}_0$ the shape tensors of the second and the reference strands, respectively. However, it can be seen that $\mathbf{R}_\phi$ in eq 17 is not, in general, unitary and therefore cannot lead to softness.

IV. Other Sources of Residual Hardness

Two other sources of residual hardening come to mind: surface anchoring of the director and cross-linked-in topological defects in the nematic director field.

Imagine a sample deforming softly in the bulk with an appropriate director rotation. If director rotation at a surface is prohibited, there must be a region of width W at the boundary where the director field changes from its surface to the bulk direction. The Frank nematic elastic energy density is $(1/2)k(\nabla n)^2 \sim K/W^2$, K is a Frank constant, $K \sim kT/a$ where a is a monomer length. In this region the elastic energy density is finite (not soft) since the director does not have its ideal direction. The scale is set by μ, the shear modulus ($\mu \sim kT/a^2L$ where L is the chain length between cross-links, giving a cross-link density of $1/a^2L$). The overall energy for a sample of area A is $E_{\text{surface}} \sim AWK/W^2 + AW\mu$, giving on minimization $W \sim (K/\mu)^{1/2} = (aL)^{1/2} \sim \bar{R}$. The transition region is on the order of a chain size $\bar{R}$. The corresponding energy is $E \sim A\bar{R}\mu$ whence the energy penalty compared with that of a nonsoft distortion is $E_{\text{surface}}/E_{\text{conventional}} \sim \bar{R}/\mathcal{L}$ with $\mathcal{L}$ the lineal dimension of the sample. This surface effect understandably vanishes in the thermodynamic limit $\bar{R}/\mathcal{L} \to 0$ and for 1 mm samples gives a ratio of $\sim 10^{-6}$.

The same qualitative argument holds for point defects; the healing length is similarly $\bar{R}$ giving a volume $\sim \bar{R}^3$ for each defect, an energy of $K\bar{R} \sim kT\bar{R}/a$ per defect, and hence an energy cost for distortion relative to that of a conventional elastomer of $(n_{\text{def}}kT\bar{R}/a)/\mu = n_{\text{def}}\bar{R}^3$, where n_{def} is the number density of defects. It would thus be of great interest to have an estimate of the defect density in otherwise perfect monodomain samples. Similar arguments can be made for line defects.

V. Conclusions

We have given explicit examples of soft deformations of nematic elastomers and shown how this anomalous liquification of an otherwise respectable solid arises. We have then calculated the tiny residual hardness that arises when there are compositional fluctuations due to copolymerization.

Acknowledgment. This research has been supported by EPSRC and Unilever Plc.

Appendix A: Hardening for a Freely Jointed Random Copolymer

We consider rod elements of types A and B of number n_A and $n - n_A$ and for simplicity of equal length l randomly making up a strand of n units. The links differ in their order parameters such that a pure chain of A would have step lengths $l_{A\parallel} = (2Q_A + 1)l/3$ and $l_{A\perp} = (1 - Q_A)l/3$ specifying its shape tensor, and similarly for B. The differing order parameters, given the same mean field seen by both types of monomer, are due to their differing structure and hence coupling to this mean field. If the average fraction of type A is $f = \langle n_A \rangle / n$ and that of B is $1 - f$, then the average shape tensor is:

$$\bar{\mathbf{l}} = f\mathbf{l}_A + (1 - f)\mathbf{l}_B$$

The deviations from the mean, for each of $\parallel$ and $\perp$ are:

$$l - \bar{l} = (n_A/n - f)(l_A - l_B) \equiv \delta l(n_A/n - f)$$

It is convenient to return to eq 13 for the free energy, rewriting it in the equivalent form:

$$\frac{2\bar{F}}{kT} = 3 + \left(\frac{\overline{\left(\frac{l_{\parallel}}{l_{\perp}}\right)}}{b^2} + b^2\overline{\left(\frac{l_{\perp}}{l_{\parallel}}\right)} - 2\right)\sin^2\theta \tag{A1}$$

We minimize over b^2, this time obtaining $b^4 = \overline{(l_{\parallel}/l_{\perp})}/\overline{(l_{\perp}/l_{\parallel})}$, which neglecting corrections of $O(1/n)$ is $b^2 = \bar{l}_{\parallel}/\bar{l}_{\perp}$ and is also to within terms of $O(1/n)$ the result obtained below eq 14. The free energy then becomes

$$\frac{2\bar{F}}{kT} = 2([\overline{(l_{\parallel}/l_{\perp})}\ \overline{(l_{\perp}/l_{\parallel})}]^{1/2} - 1)\sin^2\theta \tag{A2}$$

We then average $l_{\parallel}/l_{\perp}$ and $l_{\perp}/l_{\parallel}$ by first rewriting fractions, for instance:

$$\left(\frac{l_{\parallel}}{l_{\perp}}\right) = \frac{\bar{l}_{\parallel}[1 + (\delta l_{\parallel}/\bar{l}_{\parallel})(n_{\mathrm{A}}/n - f)]}{\bar{l}_{\perp}[1 + (\delta l_{\perp}/\bar{l}_{\perp})(n_{\mathrm{A}}/n - f)]} \tag{A3}$$

Expanding the denominator and keeping second-order terms, we can then average and obtain:

$$\overline{\left(\frac{l_{\parallel}}{l_{\perp}}\right)} = \frac{\bar{l}_{\parallel}}{\bar{l}_{\perp}}\left(1 + \overline{(n_{\mathrm{A}}/n - f)^2}\left[\left(\frac{\delta l_{\perp}}{\bar{l}_{\perp}}\right)^2 - \frac{\delta l_{\parallel}}{\bar{l}_{\parallel}}\frac{\delta l_{\perp}}{\bar{l}_{\perp}}\right] + ...\right) \tag{A4}$$

The mean-square fluctuation in composition for a random polymerization is $\overline{(n_{\mathrm{A}}/n - f)^2} = f(1 - f)/n$. This, and an expression for $\overline{(l_{\perp}/l_{\parallel})}$ analogous to eq A4, leads to (at second order)

$$\frac{2\bar{F}}{kT} = 3 + \frac{f(1-f)}{n}\left(\frac{\delta l_{\perp}}{\bar{l}_{\perp}} - \frac{\delta l_{\parallel}}{\bar{l}_{\parallel}}\right)^2\sin^2\theta \tag{A5}$$

Using the expressions for the δl in terms of the order parameters, we then obtain eq 16. Note that although in the above case we have taken the lengths of the A and B monomers to be the same, i.e., $l_{\mathrm{A}} = l_{\mathrm{B}} = l$, this need not be the case, and the more general result is:

$$\frac{2F}{kT} = 3 + \frac{f(1-f)}{n}(Q_{\mathrm{A}} - Q_{\mathrm{B}})^2\left(\frac{l_{\mathrm{A}}l_{\mathrm{B}}}{3\bar{l}_{\parallel}\bar{l}_{\perp}}\right)^2\sin^2\theta \tag{A6}$$

Appendix B: Decomposition of Soft Deformations

Any deformation at constant volume can be decomposed into a pure shear and a trivial body rotation. We now do this for the simple expression for the soft deformation λ we obtained in eq 6 in terms of the accompanying director rotation and intrinsic anisotropy $r^2 = (l_{\parallel}/l_{\perp})$. We may also write in the following form:

$$\lambda = \begin{pmatrix} \frac{1}{2}\left(1 + \frac{1}{\mathrm{r}} + \cos(2\theta)\left(1 - \frac{1}{r}\right)\right) & \frac{1}{2}\sin(2\theta)(r - 1) & 0 \\ \frac{1}{2}\sin(2\theta)\left(1 - \frac{1}{r}\right) & \frac{1}{2}(1 + r + \cos(2\theta)(1 - r)) & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{B1}$$

We note that a pure shear gives a symmetric matrix, **S**. We decompose λ:

$$\lambda = \mathbf{R}_{\phi}\cdot\mathbf{S} \tag{B2}$$

which gives a rotation through an angle ϕ:

$$\phi = \arctan\left[\frac{\sin(2\theta)(1 - \mathrm{r})^2}{(1 + \mathrm{r})^2 - (1 - \mathrm{r})^2\cos(2\theta)}\right] \tag{B3}$$

and a pure shear:

$$\left(\frac{1}{2(1 + 6r^2 + r^4 - \cos(2\theta)(1 - r^2)^2)}\right)^{1/2} \begin{pmatrix} \frac{1 + 3r^2 - (1 - r^2)\cos(2\theta)}{r} & (-1 + r^2)\sin(2\theta) \\ (-1 + r^2)\sin(2\theta) & r(3 + r^2 + (1 - r^2)\cos(2\theta)) \end{pmatrix} \tag{B4}$$

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