Thermal Fluctuations and Rubber Elasticity

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The effects of thermal elastic fluctuations in rubbery materials are examined. It is shown that, due to their interplay with the incompressibility constraint, these fluctuations qualitatively modify the large-deformation stress-strain relation, compared to that of classical rubber elasticity. To leading order, this mechanism provides a simple and generic explanation for the peak structure of Mooney-Rivlin stress-strain relation and shows good agreement with experiments. It also leads to the prediction of a phonon correlation function that depends on the external deformation.

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The term rubber (elastomer) refers to amorphous, essentially incompressible, solids that consist of a crosslinked polymer network and that can sustain large, reversible, shear deformations. It has long been understood that the elasticity of rubber is predominantly entropic, being associated with the suppression of the entropy of the polymer network by the imposed deformation. As a result rubber elasticity is characterized by a shear modulus that is proportional to temperature.

The classical theory of rubber elasticity [1,2], developed by Kuhn, Wall, Flory, Treloar, and many others around the 1940s, qualitatively accounts for the entropic nature of rubber elasticity. It is based on the crucial assumption that the junctions of polymer networks do not fluctuate in space, but nevertheless deform affinely with an imposed uniform shear strain. The entropy of the entire rubber network is then given by the sum of the entropies of each polymer chain. For a uniform shear, i.e., for a homogeneous, volume-preserving deformation Λ, the elastic free-energy density f is given by

$$f_0 = -\frac{k_B T}{V}\delta S = \frac{1}{2}\mu_0 \mathrm{Tr}\Lambda^T\Lambda, \tag{1}$$

where T is the temperature, δS is the total entropy change due to Λ, V is the volume, and $\mu_0 \approx k_B T/\xi^d$ is the entropic shear modulus in d dimensions, with ξ being the typical mesh size of the polymer network. For a *uniaxial* stretch,

$$\Lambda = (\lambda - \lambda^{-1/2})\hat{z}\,\hat{z} + \lambda^{-1/2}\mathbf{I}, \tag{2}$$

where λ is the stretch ratio along the z direction [3]. The classical theory predicts

$$f_0(\lambda) = \frac{1}{2}\mu_0\left(\lambda^2 + \frac{2}{\lambda}\right). \tag{3}$$

It has long been known that the classical theory does not work well for large deformations [1]. Its failure becomes most salient in the so-called Mooney-Rivlin plot of the stress-strain relation, in which $(df/d\lambda)/(\lambda - \lambda^{-2})$ is plotted versus $1/\lambda$. While from Eq. (3) it is clear that the classical theory predicts a horizontal line at μ_0, almost all rubbery materials, natural or synthetic, exhibit universal and nontrivial features (e.g., a peak around a compressed state), as illustrated in Fig. 1 [4].

A number of mechanisms put forward to explain these features, including polymer entanglement [5–7], non-Gaussian chain statistics, irreversible effects, internal energy effects, as well as nematic order of various types, and crystallization [1,2]. However, to date, there is no broad consensus on the nature of the dominant mechanism responsible for the deviation of rubber elasticity from the classical theory.

Our main result, Eq. (17), plotted in Fig. 1, is a generic and simple explanation for the Mooney-Rivlin data in terms of *incompressible* phonon fluctuations of the rubber network. It is based on the key observation that the classical theory is an effective mean-field theory that misses a

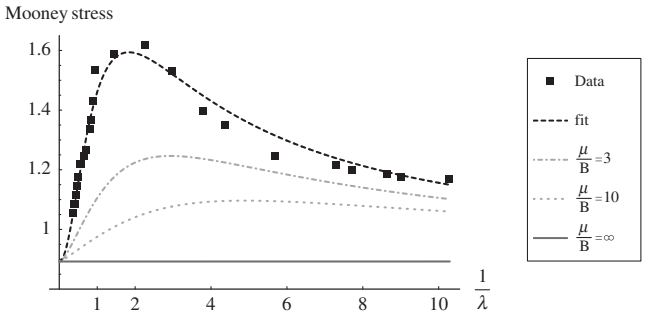

FIG. 1. The Mooney-Rivlin plot of the Mooney stress $(df/d\lambda)/(\lambda - \lambda^{-2})$ for a uniaxial shear deformation, Eq. (2), versus $1/\lambda$. While the classical theory predicts a horizontal line, real rubbery materials universally exhibit a pronounced peak feature. Squares: data from Xu and Mark [13] (unit: 10^5 Pa). Top curve: our theory fit that incorporates lowest-order phonon fluctuations on scales beyond the crosslink spacing, using Eq. (17). Fitting parameters: $B = \infty$, $\mu_0 = 8.92$, $\mu_1 = 7.10$. Also plotted are the curves for finite bulk moduli B, which are calculated using Eq. (18) and the same fitting parameters μ_0 and μ_1.

large entropic contribution to the free energy, due to thermal phonon fluctuations of the polymer network having wavelengths longer than ξ. These corrections are in fact *comparable* to the classical elastic free-energy density, Eq. (1), whose scale is given by the shear modulus $\mu_0 \approx k_B T/\xi^d$. To see this, we note that, by the equipartition theorem, each phonon mode contributes $k_B T$ to the total free energy, and that the phonon density of states is given by ξ^{-d}, set by the mesh size ξ, which is the short-scale cutoff for these long-wavelength fluctuations [8].

It is worth noting that these elastic fluctuations were previously studied by James and Guth [10] in a *phantom* network, where interactions between neighboring polymer chains are ignored. They concluded that these fluctuations are *independent* of the imposed strain deformation and therefore have *no* effect on the elasticity.

However, real rubber is nearly incompressible. So, in addition to the global volume-preserving constraint on the macroscopic distortion, i.e., $\det\Lambda = 1$, the elastic fluctuations are constrained to preserve the *local* density. As we shall show, the interplay between this local incompressibility constraint and an imposed macroscopic shear deformation alters the spectrum of phonon fluctuations. This leads to an entropic correction to the free energy that depends strongly on the imposed distortion, and thereby qualitatively modifies the stress-strain relation beyond that of the classical theory.

To go beyond classical rubber elasticity and incorporate thermal fluctuations on scale beyond ξ, we consider the Lagrangian [11] of an incompressible, homogeneous, isotropic elastic manifold (appropriate for an amorphous solid, when local heterogeneities are ignored) with the elastic energy given by the classical theory [Eq. (1)]:

$$L = \int d^d\vec{X}\left[\frac{1}{2}\rho\dot{\vec{r}}(\vec{X})^2 - \frac{1}{2}\mu_0(\vec{\nabla}\,\vec{r}(\vec{X}))^2\right], \tag{4}$$

where $\vec{r}(\vec{X})$ is the elastic configuration of a d-dimensional manifold satisfying the local incompressibility constraint

$$\det\vec{\nabla}\,\vec{r}(\vec{X}) = 1, \tag{5}$$

with $\vec{X}$ the equilibrium position of the mass point in the undeformed reference state, and ρ the mass density. Now consider a uniformly shear-strained state characterized by a deformation gradient Λ that preserves the volume, i.e., $\det\Lambda = 1$. The mass point $\vec{X}$, which was fluctuating about the position $\vec{X}$ in the unstrained state, now fluctuates around the new equilibrium position $\Lambda\cdot\vec{X}$ in the strained state.

Our task is therefore to sum over all long-wavelength elastic fluctuations in the strained state that satisfy local incompressibility. However, the highly *nonlinear* nature of the constraint, Eq. (5), is the major impediment to the analysis. The key to our progress in the solution of this problem is the resolution of the constraint (5) through the following parametrization of $\vec{r}(\vec{X})$:

$$\vec{r}(\vec{X}) = \Lambda\cdot e^{\vec{v}(\vec{X})\cdot\vec{\nabla}}\vec{X}. \tag{6}$$

It can be proven that $\vec{r}(\vec{X})$ is volume preserving *if and only if* the field $\vec{v}(\vec{X})$ is divergenceless, i.e.,

$$\vec{\nabla}\cdot\vec{v}(\vec{X}) = 0 \quad \text{or} \quad \vec{q}\cdot\vec{v}_{\vec{q}} = 0, \tag{7}$$

where the second form is the equivalent transversality (to $\vec{q}$) condition on $\vec{v}_{\vec{q}}$, the Fourier transform of $\vec{v}(\vec{X})$ [12]. The resolution of the nonlinear constraint Eq. (5) by the linear relation Eq. (7) in terms of $\vec{v}$ paves the way for a systematic treatment of thermal fluctuations in an incompressible elastomer.

Setting $\vec{v} = 0$ in Eq. (6), we find $\vec{r}_0 = \Lambda\cdot\vec{X}$, i.e., the uniformly strained reference state. For small $\vec{v}$, the exponential in Eq. (6) is

$$\vec{r}(\vec{X}) = \Lambda\cdot[\vec{X} + \vec{v}(\vec{X}) + \cdots], \tag{8}$$

identifying $\Lambda\cdot\vec{v}(\vec{X})$ with a phonon field displacement from the uniformly strained reference state $\vec{r}_0$.

The canonical momentum field $\vec{\Pi}(\vec{X})$ conjugate to $\vec{v}(\vec{X})$ is calculated in the standard way [11]. To lowest order in $\vec{v}$, we find

$$\vec{\Pi}(\vec{X}) = \frac{\delta L}{\delta\dot{\vec{v}}(\vec{x})} \approx \rho\mathbf{g}\cdot\dot{\vec{v}}(\vec{X}), \tag{9}$$

where $\mathbf{g} \equiv \Lambda^T\Lambda$ is the metric tensor.

The Hamiltonian H is related to the Lagrangian via the Legendre transformation: $H[\vec{\Pi}, \vec{v}] = \int d^d\vec{X}\Pi(\vec{X})\dot{\vec{v}}(\vec{X}) - L$. Using $\vec{r}(\vec{X})$, Eq. (8), the Lagrangian Eq. (4), and using Eq. (9) to eliminate $\dot{\vec{v}}$ in favor of the conjugate momentum $\vec{\Pi}$, to lowest (i.e., quadratic) order in $\vec{v}$ [11], we find

$$H = E_0[\Lambda] + \delta H_\Lambda[\vec{\Pi}, \vec{v}], \tag{10}$$

$$\delta H_\Lambda = \int d\vec{X}\left[\frac{1}{2\rho}\vec{\Pi}\cdot\mathbf{g}^{-1}\cdot\vec{\Pi} + \frac{\mu_0}{2}\partial_a\vec{v}\cdot\mathbf{g}\cdot\partial_a\vec{v}\right]. \tag{11}$$

Here, $E_0[\Lambda]$ is the elastic energy for the uniform strained reference state, identical to the classical theory result f_0, Eq. (1), whereas δH_Λ describes collective elastic fluctuations and depends explicitly on the uniform shear deformation Λ through the metric tensor $\mathbf{g}$.

The partition function of a macroscopically sheared rubber is then given by the following phase-space path integral:

$$Z_\Lambda = Z_\Lambda^\Pi\cdot Z_\Lambda^v = \int D\vec{\Pi}D\vec{v}\prod_{\vec{q}}\delta(\vec{q}\cdot\vec{v}_{\vec{q}})e^{-\beta\delta H_\Lambda}, \tag{12}$$

where $\beta \equiv 1/k_B T$. We note that to quadratic order in $\vec{v}$ and $\vec{\Pi}$ (which is our focus here) the partition function, Eq. (12), separates into a product of kinetic (Z_Λ^Π) and elastic (Z_Λ^v) parts. Furthermore, the incompressibility constraint applies

only to the $\vec{v}$ field but not to the canonical momentum field $\vec{\Pi}$. As a result, the momentum contribution Z_Λ^Π leads to an inconsequential strain-independent constant. We emphasize, however, that because of the nonlinear couplings between $\vec{v}$ and $\vec{\Pi}$, this property does not persist to higher orders, and in our formulation (in terms of $\vec{v}$) the momentum degrees of freedom contribute nontrivially to rubber elasticity [11].

The elastic part of the partition function is given by

$$Z_\Lambda^v = \int D\vec{v} \prod_{\vec{q}} \delta(\vec{q}\cdot\vec{v}) \exp\left[-\frac{\beta\mu_0}{2}\int_{\vec{q}} q^2 \vec{v}_{\vec{q}}\cdot\mathbf{g}\cdot\vec{v}_{-\vec{q}}\right]. \tag{13}$$

Because of the incompressibility constraint on $\vec{v}$, encoded in the δ functional, the dependence of the free energy on the imposed strain Λ cannot simply be eliminated by a change of variables. This contrasts with the aforementioned result of James and Guth [10] for a phantom network, where such a constraint and concomitantly the dependence on the imposed deformation are absent.

The structure of Z_Λ^v for the unstrained case of $\mathbf{g} = \mathbf{I}$ is identical to that of a $U(1)$ gauge field theory in the transverse gauge. Representing the δ functional by its functional Fourier representation, Z_Λ^v is easily computed via two standard Gaussian integrations:

$$\begin{aligned} Z_\Lambda^v &= \int D\alpha_{\vec{q}} D\vec{v}_{\vec{q}} e^{-\int_{\vec{q}}[(\beta\mu_0/2)q^2\vec{v}_{\vec{q}}\cdot\mathbf{g}\cdot\vec{v}_{-\vec{q}} + i\alpha_{\vec{q}}\vec{q}\cdot\vec{v}_{\vec{q}}]}, \\ &= \prod_{\vec{q}}\left(\frac{2\pi\beta\mu_0}{\mathrm{Tr}(\mathbf{P}_{\vec{q}}^L\mathbf{g}^{-1})}\right)^{1/2}, \end{aligned} \tag{14}$$

where $\mathbf{P}^L \equiv \vec{q}\,\vec{q}/q^2 = \hat{q}\,\hat{q}$ is the longitudinal projection operator onto $\hat{q}$. Ignoring irrelevant Λ-independent additive constants, we obtain the free-energy correction due to elastic fluctuations from scales longer than ξ:

$$\begin{aligned} \delta F_\Lambda &= -k_B T \ln Z_\Lambda^v = \frac{1}{2} k_B T \sum_{\vec{q}} \ln(\mathrm{Tr}\mathbf{P}^L\mathbf{g}^{-1}), \\ &= \frac{1}{2} k_B T V \xi^{-d} \Omega_d \langle \ln(\mathrm{Tr}\mathbf{P}^L\mathbf{g}^{-1})\rangle_{\hat{q}}, \end{aligned} \tag{15}$$

where $\langle\cdots\rangle_{\hat{q}}$ denotes an average over the orientation of the d-dimensional unit vector $\hat{q}$, while Ω_d is a numerical factor of order of the surface area of a d-dimensional unit sphere.

By combining this result with the classical contribution, $E_0[\Lambda] = f_0[\Lambda]$, Eq. (1), we arrive at the central result of this Letter, i.e., the elastic free-energy density of an incompressible rubber, subject to a uniform shear deformation Λ, computed to lowest-order in the thermal fluctuations:

$$f(\Lambda) = \frac{\mu_0}{2}\,\mathrm{Tr}\mathbf{g} + \frac{1}{2} T\Omega_d \xi^{-d} \langle \ln(\mathrm{Tr}\mathbf{P}^L\mathbf{g}^{-1})\rangle_{\hat{q}}. \tag{16}$$

As was argued earlier, the scale of fluctuation contribution (i.e., the second term), measured by $T\Omega_d\xi^{-d}$, is of the same order of magnitude as the classical, mean-field contribution set by the shear modulus μ_0.

For a three-dimensional uniaxially deformed system, with Λ given by Eq. (2), we have calculated the average in Eq. (16) explicitly, and thus obtain an analytical expression for $f(\lambda)$. Ignoring a λ-independent constant, we find

$$f = \frac{1}{2}\mu_0\left(\lambda^2 + \frac{2}{\lambda}\right) + \mu_1\left[\frac{\tanh^{-1}\sqrt{1-\lambda^{-3}}}{\sqrt{1-\lambda^{-3}}} - \ln\lambda\right], \tag{17}$$

where $\mu_1 \equiv 2T\Omega_d\xi^{-d}$. For compression, i.e., $\lambda < 1$, the second term should be analytically continued in such a way that it remains real and positive, namely, with $(1-\lambda^{-3})^{-1/2}\tanh^{-1}\sqrt{1-\lambda^{-3}} \to (\lambda^{-3}-1)^{-1/2}\tan^{-1}\sqrt{\lambda^{-3}-1}$, for $\lambda < 1$.

In Fig. 1 we compare our prediction for the corresponding Mooney stress, $(df/d\lambda)/(\lambda - \lambda^{-2})$, with that extracted from the stress-strain curve of Ref. [13] and find excellent agreement. The "mean field" and long-wavelength fluctuation shear moduli, μ_0 and μ_1, respectively, provide two independent fitting parameters, which only vertically translate and scale the curve in the Mooney-Rivlin plot, Fig. 1. However, the *shape* of the curve is completely determined by the fluctuation contribution (i.e., second term) of the right-hand side of Eq. (17), and thus has *no free parameters*. Comparison of Eq. (16) with experimental data on biaxial deformations (analysis of which we leave for the future) should provide more stringent test of our theory.

Our analysis can be easily extended to a more realistic system with a finite bulk modulus B. This can be done by removing the hard constraint, Eqs. (5) and (7), and adding a term $B(\vec{\nabla}\cdot\vec{v})^2/2$ to the Hamiltonian, Eq. (11), which suppresses density fluctuations. In the case of a uniaxial distortion of a compressible rubber, we find that the lowest-order fluctuation correction to the free energy becomes

$$\begin{aligned} \delta f(\lambda,\tau) = \frac{\mu_1}{2}\Bigg[&\sqrt{\frac{1+\tau/\lambda}{1-\lambda^{-3}}}\tanh^{-1}\left(\sqrt{\frac{1-\lambda^{-3}}{1+\tau/\lambda}}\right) \\ &+ \frac{1}{2}\ln(\lambda^{-2}+\tau)\Bigg], \end{aligned} \tag{18}$$

where $\tau \equiv \mu_0/B$. As illustrated in Fig. 1, this result naturally interpolates between an incompressible and phantom (classical) rubber. This result is consistent with experiments that observe a systematic reduction in the deviation from the classical theory with softening of the bulk modulus via swelling, i.e., adding solvent to the system [14].

The correlation function

$$VG_{\vec{q}}^{ab} = \langle u_{\vec{q}}^a u_{-\vec{q}}^b\rangle = \Lambda_{ai}\Lambda_{bj}\langle v_{\vec{q}}^i v_{-\vec{q}}^j\rangle \tag{19}$$

of the phonon field $\vec{u}(\vec{X}) \approx \lambda\cdot\vec{v}(\vec{X})$ [defined by Eq. (8)], relative to a macroscopically strained state $\vec{r}_0 = \Lambda\cdot\vec{X}$, can also easily be computed. For an incompressible rubber, a

Gaussian integration with the Boltzmann weight from Eq. (14) gives

$$G^{ab}_{\vec{q}} = \frac{k_B T}{\mu_0 q^2}\left(\delta_{ab} - \frac{\Lambda^{-1}_{ia}\Lambda^{-1}_{jb}\hat{q}_i\hat{q}_j}{\mathrm{Tr}\mathbf{P}^L\mathbf{g}^{-1}}\right). \quad (20)$$

There is a small caveat, however. We have been labeling the mass points in the deformed state $\vec{r}_0 = \Lambda \cdot \vec{X}$ by their undeformed equilibrium coordinate $\vec{X}$, which is conjugate to the wave vector $\vec{q}$. However, the wave vector $\vec{p}$ probed by scattering experiments is the one conjugate to the deformed equilibrium position $\vec{r}_0 = \Lambda \cdot \vec{X}$. These two vectors are related via

$$(\vec{p}, \Lambda \cdot \vec{X}) = (\vec{q}, \vec{X}) \rightarrow \vec{q} = \Lambda^T \cdot \vec{p}, \quad (21)$$

where $(\cdots)$ denotes the inner product of two d-dimensional vectors. Therefore, the phonon correlation function, as a function of the *physical* wave vector $\vec{p}$ is given by Eq. (20) with $\vec{q}$ expressed in term of $\vec{p}$ through Eq. (21). This leads to

$$G^{ab}_{\vec{p}} = \frac{T/\mu_0}{\vec{p}\cdot\Lambda\Lambda^T\cdot\vec{p}}(\delta_{ab} - \hat{p}_a\hat{p}_b) \propto P^T_{ab}(\vec{p}), \quad (22)$$

which is proportional to the transverse projector, as expected from incompressibility. The predicted anisotropic strain-dependence provides an independent test of the theory.

In this Letter we have demonstrated the importance of thermal fluctuations for the elasticity of isotropic rubber, particularly in the large-deformation regime. It is not difficult to see, however, that the same general mechanism extends to all incompressible soft solids, such as liquid crystalline elastomers. Our current analysis is limited to the lowest order. Because the effective coupling constant is of order unity, we expect higher-order corrections to be quantitatively important. However, as illustrated in Fig. 1, the lowest-order contributions already capture the essential effects of thermal fluctuations on rubber elasticity. Our formalism provides a systematic approach for addressing these higher-order contributions. We hope that our work will stimulate further studies in this direction.

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[1] L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon Press, Oxford, 1975).
[2] M. Rubinstein and R. H. Colby, *Polymer Physics* (Oxford University Press, New York, 2003).
[3] Note that $\lambda < 1$ means a uniaxial compression.
[4] For sufficiently small λ^{-1}, the experimental Mooney stress curve should turn up again, due to the finite extensibility of polymer chains. This part of the data is not shown here.
[5] S. F. Edwards and T. A. Vilgis, Rep. Prog. Phys. **51**, 243 (1988).
[6] M. Rubinstein and S. Panyukov, Macromolecules **35**, 6670 (2002).
[7] S. Kutter and E. M. Terentjev, cond-mat/0106371.
[8] In an ordinary solid, the free-energy contribution due to long-wavelength fluctuations is also $O(T/\xi^d)$, but in contrast (at low T, below the solid's melting temperature) is much smaller than the elastic part set by the elastic constants that have *energetic* origin [9].
[9] D. S. Fisher, Phys. Rev. B **26**, 5009 (1982).
[10] H. M. James and E. Guth, J. Chem. Phys. **11**, 455 (1943).
[11] Although it is perhaps surprising for this classical (i.e., nonquantal) statistical mechanics problem (where one would expect kinetic degrees of freedom to inconsequentially decouple), a full phase-space formulation is convenient here. In it, the functional integration measure $D\vec{\Pi}_{\vec{r}}D\vec{r}$ is invariant under canonical transformations, thereby allowing us to perform the nonlinear transformation to $\vec{v}$, Eq. (6) (required to resolve the incompressibility constraint), without introducing a highly nonlinear (in $\vec{v}$) functional Jacobian. The price for this is a conjugate momentum, $\vec{\Pi}_{\vec{v}}$, that nonlinearly couples to $\vec{v}$, and therefore cannot in general be integrated out.
[12] $\vec{r}(\vec{X})$ is a volume-preserving automorphism of three-dimensional Euclidean space $E(3)$. The collection of all such functions forms a subgroup of the diffeomorphism group Diff$[E(3)]$, an infinite-dimensional non-Abelian, noncompact, Lie group. The mathematical implication of Eq. (6) is that the vector field $\vec{v}(\vec{X})$ is an element of the corresponding infinite-dimensional Lie algebra, and therefore generates an incompressible (i.e., volume-preserving) flow $\vec{r}(\vec{X})$. For an arbitrary, volume-preserving $\vec{r}(\vec{X})$, there may not exist a vector field $\vec{v}(\vec{X})$ such that Eq. (6) holds. However, one can always find such a $\vec{v}(\vec{X})$ if $\vec{r}(\vec{X})$ is sufficiently close to $\vec{X}$. At relatively low temperatures, therefore, we expect that the summation over all volume-preserving deformations $\vec{r}(\vec{X})$ can be replaced by one over all incompressible flows $\vec{v}(\vec{X})$.
[13] P. Xu and J. E. Mark, Rubber Chem. Technol. **63**, 276 (1990).
[14] See, for example, Chap. 5 of Ref. [1] for a review.