Cross-linking patterns and their images in swollen and deformed gels

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July 13, 2015

Abstract

Using the theory of elasticity of polymer gels we show that large-scale cross-link density patterns written into the structure of the network in the melt state, can be revealed upon swelling by monitoring the monomer density patterns. We find that while isotropic deformations in good solvent yield magnified images of the original pattern, anisotropic deformations distort the image (both types of deformation yield affinely stretched images in \( \theta \) solvents). We show that in ordinary solids with spatially inhomogeneous profile of the shear modulus, isotropic stretching leads to distorted density image of this profile under isotropic deformation. Using simple physical arguments we demonstrate that the different response to isotropic stretching stems from fundamental differences between the theory of elasticity of solids and that of gels. Possible tests of our predictions and some potential applications are discussed.
1 Introduction

Polymer networks are unique soft solids which can be significantly deformed without irreversible damage to their structure. A network is formed by cross-linking a melt or a semidilute solution of polymer chains. Once a homogeneous (on length scales large compared to its “mesh” size) network is formed, one can generate large-scale patterns in it by further cross-linking, followed by swelling (and possibly stretching) of the network, resulting in a gel inhomogeneously swollen by solvent. This can be done, for example, by adding light-sensitive cross-links to a transparent network. Focusing a laser beam in regions inside the gel one can “write” information into gel structure in the form of 2D or 3D patterns of cross-linking density. In this paper we show that although such information is hidden at preparation conditions, it can be recovered by swelling the gel since unobservable variations of cross-link density in the melt are transformed into observable variations of monomer density in the swollen gel.

Regions of a gel with increased cross-link concentration can be considered as inclusions with enhanced elastic modulus. If such inclusions deform differently from polymer matrix, as in case of any normal elastic solids, they would induce elastic stresses in the gel and initial pattern would be significantly distorted due to long range character of elastic interactions. This scenario determines, for example, the elastic properties of amorphous polycrystalline solids but it does not apply to polymer gels, because of the unusual character of gel elasticity. We show that in swollen gels that are isotropically stretched by absorption of solvent, the observed monomer density pattern is not distorted and is simply an affinely stretched variant of the initial cross-linking pattern. Such gels can serve as a magnifying glass that enlarges the initially written pattern without distorting its shape. The corresponding magnification factor can be very large in case of super-elastic networks.
2 Free energy of a gel with cross-linking density pattern

In this paper we use the simplest mean field model of a gel with free energy [1,2]:

\[
A = \int \left( \frac{G(x_0)}{2} \sum_{ij} F_{ij}^2 + f[\rho(x_0)] \right) dx_0
\]

(1)

Here \( \rho(x_0) \) is monomer density as function of coordinates \( x_0 \) in preparation state. We assume that the gel was initially cross-linked in a polymer melt and then a pre-programmed pattern in cross-link concentration (i.e., a well-defined region of higher cross-link density compared to that of the surrounding network) is created in the network using, say, a light-sensitive cross-linking technique (the case of cross-linking in semi-dilute solution in good solvent is analyzed in SI). Here \( G(x_0) \) is the polymer contribution to the elastic modulus of the cross-linked melt (which is proportional to the local cross-link density)

\[
G(x_0) = \bar{G} + \tilde{G}(x_0)
\]

(2)

and \( \tilde{G}(x_0) \) represents the variations of cross-link density introduced by the second cross-linking step (Fig. 1a). \( f(\rho) \) is the osmotic (interaction) part of the free energy of the gel, with monomer density \( \rho \). \( F \) is the deformation gradient tensor

\[
F_{ij} = \frac{\partial x_i}{\partial x_0 j}
\]

(3)

and \( x \) are coordinates of deformed gel. It is convenient to assume that the gel is deformed with respect to preparation state in two stages:

\[
F_{ij} = \sum_l F_{il}^{\lambda} F_{lj}^{\lambda}
\]

(4)

Thus, the gel is first stretched with respect to preparation state by factors \( \lambda_i \) along axes \( i \). For such a deformation \( x = \lambda \cdot x_0 \) with components \( x_i = \lambda_i x_{0i} \) and we get

\[
F_{ij}^{\lambda} = \lambda_i \delta_{ij}, \quad \rho = \bar{\rho} = \frac{\rho_0}{\prod_i \lambda_i}
\]

(5)

where \( \rho_0 \) is the uniform monomer density in the undeformed state of preparation (Fig. 1b). Notice that the coordinates \( x \) describe a stretched network

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with inhomogeneous cross-link density but a homogeneous monomer density (Figs. 1c and d).

Even though such a homogeneous (in monomer density) state does not minimize the free energy and therefore is not an equilibrium state of the deformed gel, we use it as a reference state. The true equilibrium state of the deformed network has an inhomogeneous monomer density profile and is defined by introducing a displacement field $u(x)$ defined with respect to the above reference state:

$$x' = x + u(x)$$  \hspace{1cm} (6)

and we get gradient tensor and monomer density as function of coordinates $x$

$$F_{ij}^u = \delta_{ij} + \frac{\partial u_i}{\partial x_j}, \quad \rho(x) = \frac{\bar{\rho}}{\det(F_{ij}^u)},$$  \hspace{1cm} (7)

$$\det(F_{ij}^u) \simeq 1 + \sum_i \frac{\partial u_i}{\partial x_i}$$  \hspace{1cm} (8)

Minimizing the free energy in Eq. (1) with respect to displacements $u$ at the preparation state (all $\lambda_i = 1$) we conclude that in a melt the cross-links and the monomers will remain at their previous positions and the elastic reference state will not change after relaxation. We conclude that
information about the pattern written on network structure is hidden in preparation state and can only be revealed after swelling.

3 What is the equilibrium density profile?

In a swollen state the monomer density is small and the interaction energy can be expanded as \( f(\rho) \simeq k_B T B \rho^2 / 2 \), where \( k_B \) is Boltzmann constant, \( T \) is temperature and \( B \) is second virial coefficient. Expanding the free energy in powers of \( u \) and integrating over the volume of the undeformed network with measure \( dx_0 = dx / \prod_i \lambda_i \) we get

\[
\Delta A = \int \left[ \tilde{G}(\lambda^{-1} \cdot x) \sum_i \lambda_i^2 \frac{\partial u_i}{\partial x_i} + \frac{\tilde{G}}{2} \sum_{ij} \left( \lambda_j \frac{\partial u_i}{\partial x_j} \right)^2 \right] \frac{dx}{\prod_i \lambda_i}, \quad K_{os} = k_B T B \tilde{\rho}^2. \tag{9}
\]

The equilibrium deformation of the gel is found by minimizing this free energy. Its variation is

\[
\delta A = \int \left( - \sum_i \delta u_i \lambda_i^2 \frac{\partial \tilde{G}}{\partial x_i} - \tilde{G} \sum_{ij} \lambda_j^2 \frac{\partial^2 u_i}{\partial x_j^2} \delta u_i \right. \\
\left. - K_{os} \sum_{ij} \frac{\partial^2 u_i}{\partial x_i \partial x_j} \delta u_i \right) \frac{dx}{\prod_i \lambda_i} \tag{10}
\]

and therefore, the minimum condition is

\[
- \lambda_i^2 \frac{\partial \tilde{G}}{\partial x_i} - \tilde{G} \sum_j \lambda_j^2 \frac{\partial^2 u_i}{\partial x_j^2} - K_{os} \sum_j \frac{\partial^2 u_i}{\partial x_i \partial x_j} = 0 \tag{11}
\]

We are interested only in variations of monomer density

\[
\frac{\tilde{\rho}(x)}{\bar{\rho}} \simeq - \sum_i \frac{\partial u_i(x)}{\partial x_i} \tag{12}
\]

where \( \bar{\rho} \) is average density. Taking the gradient of both sides of Eq. (11) we obtain an equation for the variations of monomer density

\[
\sum_i \lambda_i^2 \frac{\partial^2 \tilde{G}(\lambda^{-1} \cdot x)}{\partial x_i^2} - \sum_i \gamma_i^2 \frac{\partial^2 \bar{\rho}(x)}{\partial x_i^2} \frac{\tilde{\rho}(x)}{\bar{\rho}} = 0 \tag{13}
\]
where
\[ \gamma_i^2 = G\lambda_i^2 + K_{\text{os}} \] (14)

The solution of this equation

\[ \frac{\tilde{\rho}(x)}{\bar{\rho}} = \sum_i \lambda_i^2 \frac{\partial^2}{\partial x_i^2} \int g \left[ \gamma^{-1} \cdot (x - y) \right] \tilde{G} \left( \lambda^{-1} \cdot x \right) \frac{dy}{\prod_j \gamma_j} \] (15)

is expressed through Green’s functions of the Laplace equation in 2 and 3 dimensions, respectively:

\[ g_{2D}(x) = \frac{1}{4\pi} \ln \sum_i x_i^2, \quad g_{3D}(x) = -\frac{1}{4\pi \sqrt{\sum_i x_i^2}} \] (16)

In case of isotropically stretched/swollen gel with all \( \lambda_i = \lambda \) the equilibrium monomer density depends on local cross-link concentration,

\[ \frac{\tilde{\rho}(x)}{\bar{\rho}} = \frac{\lambda^2}{\gamma^2} \tilde{G} \left( \frac{x}{\lambda} \right) \] (17)

We conclude that under isotropic deformation such as swelling, the monomer density produces an undistorted, uniformly stretched image of the pattern of cross-link density originally “written” on the homogeneous network (compare Figs. 1a and e).

Equilibrium displacement is expressed through the variation of monomer density, Eq. (17), as

\[ u_i(x) = -\frac{\partial}{\partial x_i} \int g(x - y) \frac{\tilde{\rho}(y)}{\bar{\rho}} dy \] (18)

We conclude that although density variations in isotropically deformed gels are strictly local, there is long-range strain field decaying as power law of the distance \(|x - y|\). This strain induces a stress distribution in the gel, which can be observed by measuring the birefringence of transmitted light (stress-optical law [3]).

In anisotropically deformed networks the pattern is strongly distorted (compare Figs. 1a and f) and \( \tilde{\rho}(x) \) decays as power law of a distance \(|x - y|\) from the localized cross-link density inhomogeneity \( \tilde{G}(y) \). Observe that variations of monomer density are largest along the direction of stretching. This effect is closely related to the well known “butterfly” picture in contour plots of neutron scattering from random inhomogeneities of network structure in anisotropically deformed swollen gels [4].
4 What is the difference between deformation of gels and elastic solids?

In order to understand the difference between gels and normal solids we recall that the free energy of any solid is a functional of the nonlinear strain tensor \( u_{ik} \) [5],

\[
2u_{ik} = \sum_j F_{ij}F_{kj} - \delta_{ik} = \frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} + \sum_j \frac{\partial u_i}{\partial x_j} \frac{\partial u_k}{\partial x_j}
\]  (19)

While the last term is usually neglected in the linear theory elasticity of solids because solids behave elastically only under small deformations, it can be shown that only this nonlinear term contributes to the elasticity of gels and that the elastic part of the free energy of gels (Eq. (1)) is linear in this nonlinear strain [6, 7]. Physically, the difference between elastic energy of a solid, which is a quadratic form in the linear strain and of a gel, which is linear in the nonlinear strain tensor, stems from the fact that while in solids there is a stress-free state of equilibrium (crystal lattice) that minimizes the energy of interaction between the atoms, the equilibrium state of gels is not stress-free. Polymer networks are made of entropic springs and, in the absence of osmotic pressure due to permeation by good solvent or due to excluded volume interactions in the melt state, such networks would collapse to the size of a single spring. The finite length of entropic springs in the swollen gel is the result of osmotic pressure which can be replaced by equivalent isotropic stretching forces that act on the outer boundaries of the gel [8].

The difference between gels and solids becomes apparent when considering two simple toy models of heterogeneous gel and solid as two Hookean springs with moduli \( k_1 \) and \( k_2 \), connected in series as in Fig. 2:

**a) Gel model:** Osmotic pressure is represented by a force \( f_{os} \) applied to free ends of the connected springs. In the presence of this force the equilibrium lengths of the Gaussian springs become \( r_{1i}^{eq} = f_{os}/k_1 \) and \( r_{2i}^{eq} = f_{os}/k_2 \), and if we apply additional force \( f \), each of the springs will deform affinally with distance \( r_1 + r_2 \) between the ends to which the force is applied (“boundaries” of the system):

\[
r_1 = \lambda r_1^{eq}, \quad r_2 = \lambda r_2^{eq}, \quad \lambda = \frac{r_1 + r_2}{r_1^{eq} + r_2^{eq}}
\]  (20)

**b) Solid model:** The springs of a “solid” have equilibrium lengths \( r_1^{eq} \) and \( r_2^{eq} \) in the stress-free state. During stretching due to force \( f \) applied to the
ends of the two-spring system, such a solid deforms nonaffinely:

\[
\begin{align*}
  r_1 &= r_1^{eq} + (\lambda - 1) (r_1^{eq} + r_2^{eq}) \frac{k_2}{k_1 + k_2}, \\
  r_2 &= r_2^{eq} + (\lambda - 1) (r_1^{eq} + r_2^{eq}) \frac{k_1}{k_1 + k_2},
\end{align*}
\]  

(21)

with the soft spring \((k_1 < k_2)\) stretched more than the rigid one.

These two simple toy models illustrate why under isotropic deformations, cross-linking density patterns in gels are stretched affinally, whereas soft regions in solids would undergo larger deformation compared to more rigid regions, thus distorting the original pattern.

5 Discussion

We studied the combined effect of swelling and deformation on inhomogeneous networks, prepared by cross-linking a melt of polymer chains. It is well-known that cross-link density heterogeneities that have no effect on the monomer density in the state of preparation (a melt or a concentrated polymer solution), can be revealed by swelling the gel and observing the enhancement of light, x-ray and neutron scattering from the resulting monomer density inhomogeneities \[9-12\]. In this paper we focused on a related phenomenon, namely that when large-scale cross-link density patterns are written into the network structure, the hidden image can be revealed by swelling and stretching the gel and observing the corresponding patterns of monomer density. Using the mean field theory of elasticity of polymer gels we showed
that stretching/swelling in good solvent acts as a magnifying glass: while isotropic stretching reproduces an enlarged but otherwise undistorted version of the original pattern, anisotropic stretching distorts this pattern, see figure 1.

We compared these results with those obtained for ordinary elastic solids with inhomogeneous elastic moduli and found that in this case even isotropic deformations lead to distorted patterns. We showed that the fundamental difference between response of inhomogeneous gels and solids to isotropic stretching can be traced back to the fact that unlike regular springs that have an equilibrium length even in the absence of stress, the equilibrium length of entropic springs is entirely determined by the osmotic forces that isotropically stretch the polymer gel.

Finally, we would like to comment on the possibility of experimental verification and on possible applications of our results. In most applications involving gels such as biomimetic sensors, actuators and artificial muscles [13], macroscopically inhomogeneous (layered) gels undergo shape transitions when the thermodynamic conditions are changed or in response to application of external fields [14]. In our case, the cross-link density pattern imprinted into the gel structure by, say, activation of light-sensitive cross-links, can be microscopic (micron size) and therefore would have little effect on the shape of the gel. Upon swelling and/or isotropic stretching in good solvent, the magnified density pattern can be imaged on a light-sensitive screen. The contrast can be significantly enhanced by stretching the entire gel in poor solvent or by focusing a laser beam on the localized pattern and heating it, resulting in local change of the quality of solvent. Finally, the sensitivity of the image to quality of solvent (the distortion under anisotropic deformation disappears in \( \theta \) solvent - see SI) can be useful for sensor devices.

Acknowledgments
YR’s research was supported by the I-CORE Program of the Planning and Budgeting committee and the Israel Science Foundation, and by the US-Israel Binational Science Foundation.

Supporting Information.
In the SI we show that patterns obtained by cross-linking a semi-dilute polymer solution, deform affinely (non-affinely) under isotropic (anisotropic) deformation, just like in the case of cross-linking in the melt. We then analyze how the pattern deforms under several different solvent conditions. We
show that the pattern always stretches affinely in a $\theta$-solvent, even under anisotropic deformations. Since the contrast between the high and the low monomer density regions can be significantly enhanced in a poor solvent we proceed to analyze the density profiles in gels that are isotropically stretched in mildly poor solvents (at lower solubility, such stretched gels will undergo a transition into a strongly inhomogeneous state characterized by the appearance of dense filamentous structures [15]). We find that when the amplitude of cross-link density variations is sufficiently low, the image stretches affinely with the isotropic deformation but that for larger density contrasts the image becomes distorted, especially near the edges and corners of the pattern.

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**Supplementary Information to:**

**Cross-linking patterns and their images in swollen and deformed gels**

**SI 1. Gel free energy in a good solvent**

Consider a gel prepared in a good solvent at the monomer density $\rho_0$ that is swollen to density $\rho$. Its free energy is the sum of elastic and osmotic contributions. The osmotic pressure $\pi$ of the gel in a good solvent increases proportionally to the $9/4$ power of monomer density $\rho$ \[ \pi \simeq (k_B T/b^3) (\rho b^3)^{9/4} \] (S1)

where $k_B$ is Boltzmann constant, $T$ is temperature and $b$ is monomer size. The osmotic part $A_{os}$ of the free energy per polymer chain between network junctions is proportional to the free energy density ($\sim \pi$) divided by the number of chains per unit volume ($\rho/N$), where $N$ is the chain degree of polymerization:

$$ A_{os}^\text{ch} \simeq \pi/(\rho/N) \simeq k_B TN (\rho b^3)^{5/4} \] (S2)

The dimension of the chain along the main axis $\alpha$ of deformation is $R_\alpha = \Lambda_\alpha R_0$, where $\Lambda_\alpha$ is deformation factor along this axis (defined as eigenvalue of local deformation gradient tensor $F$) and $R_0$ is the chain size in the state at which the gel was formed. The elastic free energy per chain is

$$ A_{el}^\text{ch} \simeq k_B T \sum_{\alpha} \left( \frac{R_\alpha}{R_{fl}} \right)^2 \simeq k_B T \left( \frac{R_0}{R_{fl}} \right)^2 \sum_{\alpha} \Lambda_\alpha^2 \] (S3)

where $R_{fl}$ is the amplitude of fluctuations of the chain in the deformed state. In a heterogeneous network the direction of the triad of deformation axes $\alpha$ depends on its position, and the sum of squares of local deformation factors in Eq. (S3) can be rewritten through the deformation gradient tensor $F$ as

$$ \sum_{\alpha} \Lambda_\alpha^2 = \sum_{ij} F_{ij}^2 \] (S4)

Since the mean-square amplitude of chain fluctuations is proportional to the mean-square polymer size at semi-dilute good solvent conditions and scales
with monomer density as $R_{ji}^2 \sim \rho^{-1/4}$, while the mean-square chain size in the preparation conditions scales as $R_0^2 \sim \rho_0^{-1/4}$, the elastic free energy per chain is

$$A_{\text{el}} \simeq k_BT \left( \frac{\rho}{\rho_0} \right)^{1/4} \sum_{ij} F_{ij}^2$$  \hspace{1cm} (S5)

At the equilibrium swelling ($\rho = \rho_{\text{eq}}$) in the absence of additional deformations the total free energy of the gel per chain is:

$$A_{\text{ch}} = A_{\text{el}} + A_{\text{osm}} \simeq k_BT \left[ N \left( \frac{\rho_{\text{eq}} b^3}{\rho_0} \right)^{5/4} + \left( \frac{\rho_0}{\rho_{\text{eq}}} \right)^{5/12} \right]$$  \hspace{1cm} (S6)

and it is minimized at the density \[2\]

$$\rho_{\text{eq}} \simeq \left( \frac{\rho_0 b^3}{b_3 N^{3/5}} \right)^{1/4} \hspace{1cm} (S7)$$

corresponding to maximum swelling ratio

$$\lambda_{\text{eq}} = \left( \frac{\rho_0}{\rho_{\text{eq}}} \right)^{1/3} \simeq \left( \frac{\rho_0 b^3}{b_3} \right)^{1/4} N^{1/5} \hspace{1cm} (S8)$$

Note that similar expression for $\lambda_{\text{eq}}$ is obtained in mean field model of a gel with second virial coefficient $B \simeq b^3$, see main text. This conclusion can also be extended to our solution of the image storing problem. Since both elastic (Eq. (S5)) and osmotic (Eq. (S2)) terms in the gel free energy are multiplied by the same scaling factor $(\rho/\rho_0)^{1/4}$ such scaling renormalization does not change the results obtained for the mean field model.

**SI 2. How does the pattern change in different solvent conditions?**

**$\theta$-solvent**

In a $\theta$-solvent the second virial coefficient vanishes ($B = 0$) and equation

$$\frac{\tilde{\rho}(\mathbf{x})}{\tilde{\rho}} = \sum_i \lambda_i^2 \frac{\partial^2}{\partial x_i^2} \int g \left[ \gamma^{-1} \cdot (\mathbf{x} - \mathbf{y}) \right] \tilde{G} (\lambda^{-1} \cdot \mathbf{x}) \frac{d\mathbf{y}}{\prod_j \gamma_j}$$  \hspace{1cm} (S9)

reproduces without distortion affinely stretched initial pattern

$$\frac{\tilde{\rho}(\mathbf{x})}{\tilde{\rho}} = \tilde{G} (\lambda^{-1} \cdot \mathbf{x}) / \tilde{G},$$  \hspace{1cm} (S10)

even for anisotropically stretched gels (small deviations from affinity are expected because of the non-vanishing third virial coefficient).
Poor solvent

Strong enhancement of monomer density contrast can be obtained by placing the gel (with fixed boundaries – otherwise it would collapse) in a poor solvent with negative second virial coefficient $B < 0$. In case of very poor solvent with

$$\gamma^2 = \tilde{G}\lambda^2 + k_BT\bar{\rho}^2 < 0$$  \hspace{1cm} (S11)$$

the gel becomes unstable with respect to formation of domains with different monomer density \[3\]. Below we consider the case of poor solvent close to $\theta$-conditions with small $B < 0$ and positive $\gamma^2 > 0$.

At small $\gamma^2$ the amplitude of density variations $\tilde{\rho} (x)$ can be significantly increased because of the small denominator in equation

$$\frac{\tilde{\rho} (x)}{\bar{\rho}} = \frac{\lambda^2}{\gamma^2} \tilde{G} \left( \frac{x}{\lambda} \right)$$  \hspace{1cm} (S12)$$

and we have to take into account corrections due to second order in $u$ term

$$\Delta (u) \simeq \sum_{ij} \left( \frac{\partial u_i}{\partial x_i} \frac{\partial u_j}{\partial x_j} - \frac{\partial u_i}{\partial x_j} \frac{\partial u_j}{\partial x_i} \right)$$  \hspace{1cm} (S13)$$

in expression for monomer density,

$$\rho (x) = \frac{\bar{\rho}}{\text{det} \left( F_{ij}^u \right)}$$  \hspace{1cm} (S14)$$

where

$$\text{det} \left( F_{ij}^u \right) = 1 + \sum_i \frac{\partial u_i}{\partial x_i} + \Delta (u)$$  \hspace{1cm} (S15)$$

To first order in $\Delta$ we find

$$\frac{\tilde{\rho} (x)}{\bar{\rho}} \simeq \frac{\lambda^2}{\gamma^2} \left[ \tilde{G} \left( \frac{x}{\lambda} \right) - \tilde{G} \Delta (u) \right]$$  \hspace{1cm} (S16)$$

where the equilibrium displacement in $\Delta (u)$ is determined as

$$u_i (x) \simeq -\frac{\lambda^2}{\gamma^2} \frac{\partial}{\partial x_i} \int g(x-y) \tilde{G} \left( \frac{y}{\lambda} \right) dy$$  \hspace{1cm} (S17)$$

We conclude that the correction term in Eq. \[S16\] enhances the contrast between the high and the low monomer density regions of the profile (Fig. S1). This effect is the mostly pronounced near the corners of the pattern where several edges converge and it leads to distortion of the otherwise affinely stretched profile at these points.
Figure S1: Density profile in poor solvent for initial cross-link concentration shown in Fig. 1a).

SI 3. Random heterogeneities

Frozen-in random heterogeneities of network structure can change the image beyond recognition [4]. The free energy of a gel with frozen-in heterogeneities was derived in Ref. [5]. The only source of heterogeneities in the melt with fixed monomer density is statistical distribution of cross-links in the state of preparation that arises as the consequence of the random process of cross-linking. This frozen-in distribution is described by an additional contribution to the free energy:

$$\Delta A_n = - \int \sum_{ij} f_{ij}(\mathbf{x}) \frac{\partial u_i}{\partial x_j} d\mathbf{x}$$  \hspace{1cm} (S18)

where $f_{ij}(\mathbf{x})$ is random Gaussian function of coordinate $\mathbf{x}$, characterized by correlation function

$$f_{ij}(\mathbf{x}) f_{kl}(\mathbf{x}') \simeq (k_B T)^2 \tilde{G} \delta(\mathbf{x} - \mathbf{x}') \delta_{ik} \delta_{jl}$$  \hspace{1cm} (S19)

Comparing the amplitude of frozen-in fluctuations on a scale $R$ with variations of elastic modulus $\tilde{G}$ on this scale we conclude that the contribution of
frozen-in heterogeneities can be neglected if

\[ \frac{\bar{G}}{G} \gg \frac{1}{(\bar{c}R^3)^{1/2}} \]  

(S20)

where \( \bar{c} \) is average cross-link concentration and thus, frozen-in heterogeneities have no influence on large-scale patterns. The suppression of frozen-in heterogeneities of monomer density is due to strong overlap of network chains [6].

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