STATISTICAL PHYSICS OF SOFT RANDOM SOLIDS: VULCANIZATION, HETEROGENEITY, AND ELASTICITY

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DISSERTATION

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Abstract

Soft random solids are formed at an equilibrium phase transition — the gelation transition — from a liquid to a random solid state, driven by random permanent chemical linking of the constituent molecules. Such solids are characterized by their heterogeneous structure and remarkable elasticity. The most prominent example of soft random solids, rubber, is composed of polymers, crosslinked to form a network, and has an extraordinarily large reversible deformability.

The first part of this thesis, Chapter 2, presents a simple and physically intuitive approach to the gelation/vulcanization transition — the so-called cavity method, borrowed from spin glass theory. This cavity approach confirms results that have been obtained previously via replica mean-field theory, such as the dependence of the gel fraction and the distribution of localization lengths on the density of links. It also sheds new light on the physical origin of these dependences.

In the second part of this thesis, Chapters 3, 4, and 5, spatial heterogeneity in the elastic properties of soft random solids is examined via vulcanization theory. The spatial heterogeneity in the structure of soft random solids is a result of the fluctuations locked-in at their synthesis, which also brings heterogeneity in their elastic properties. Vulcanization theory studies semi-microscopic models of random-solid-forming systems, and applies replica field theory to deal with their quenched disorder and thermal fluctuations. The elastic deformations of soft random solids are argued to be described by the Goldstone sector of fluctuations contained in the vulcanization theory, associated with a subtle form of spontaneous symmetry breaking that is associated with the liquid to random solid transition. The resulting free energy of these Goldstone modes can be reinterpreted as arising from a phenomenological description of an elastic medium with quenched disorder. Through this comparison, we arrive at the statistics of the quenched disorder of the elasticity of soft random solids, in terms of residual stress and Lamé-coefficient fields. In particular, there are large residual stresses in the equilibrium reference state, and the disorder correlation functions involving the residual stress are found to be long-ranged and governed by a universal parameter that also gives the mean shear modulus.
To my grandmother, my parents, and my husband.
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List of Abbreviations

SSB Spontaneous Symmetry Breaking
RLPM Randomly Linked Particle Model
HRS Higher Replica Sector
LRS Lower Replica Sector
1RS One Replica Sector
0RS Zero Replica Sector
1.1 The physics of soft random solids and the vulcanization transition

1.1.1 Random solids

Random solids, or amorphous solids [1], are well-defined solids from the mechanical perspective. Macroscopically, it costs energy to make a shear deformation of random solids; however, microscopically, the molecular structures of random solids exhibit none of the long-range order of crystals, which makes them resemble liquids, at least instantaneously.

The physics of random solids is remarkably rich, and spans widely different areas of modern physics, such as phase transitions and critical phenomena, nonequilibrium statistical mechanics, the quantum mechanics of electronic structure, biophysics, etc.

A large category of random solids, generally grouped under the name glasses, lead to one of the most intriguing problems in modern condensed matter physics [2]. In principle, given a sufficiently high cooling-rate, any liquid can be made into a glass (i.e., vitrified) [3, 4, 5]. Upon rapid cooling, the supercooled liquid becomes more and more viscous, and ultimately falls out of equilibrium on experimentally achievable time-scales at the so-called glass temperature $T_g$. It is still an open question whether there is an underlying equilibrium thermodynamic phase transition at the glass transition. The resulting glass phase has striking physical properties, especially at low temperatures, which exhibit a fascinating universality in the heat capacity and thermal conductivity.

Our study of random solids focuses on a different category: soft random solids. Unlike glasses, soft random solids are formed by the permanent random chemical linking of the constituent molecules, and the transition from liquid to soft random solid is an equilibrium phase transition, driven by the density of links. Soft random solids include rubber [6], formed by crosslinked polymer networks, and chemical gels [7], formed by networks of small molecules connected by covalent bonds. The equilibrium character of the transition to the soft random solid state enables one to use powerful tools of equilibrium statistical physics, such as the theory of criticality and symmetry breaking, to
investigate the transition to, and properties of, the soft random solid state. These theoretical developments, which we group together under the heading *vulcanization theory* [8, 9], may also serve as a simple universal field-theoretic model of more general classes of random solids, inasmuch as they capture the basic spontaneous symmetry breaking at the random solidification transition. Thus, it is not out of the question that they will also shed some light on the theory of true glasses.

We shall take rubber as our prototype for the discussion of soft random solids. Rubber is formed by adding permanent crosslinks at random between instantaneously nearby monomers in melts or solutions of flexible polymers. When the density of the crosslinks exceeds the percolation limit, an infinite cluster forms, a nonzero fraction of the polymers become spatially localized (at least in dimensions greater than two [10, 11]), and the network acquires a rigidity to shear deformations. ¹ This event is commonly called the “vulcanization transition” [8, 9] or “gelation”. ²

1.1.2 Basics of polymer physics

Linear polymers are the building blocks of rubber. These polymers are very long, covalently bonded, macromolecules made up of many small groups of atoms [13, 14, 15]. The repeating small groups are called monomers. A typical polymer can contain $10^2 \sim 10^{10}$ monomers, and this number of repeating units is called degree of polymerization $N_{DP}$. In particular, natural rubber (*Hevea* rubber) is a polymer of the isoprene monomer $C_5H_8$.

The spatial shape, *i.e.*, the “conformation” of a polymer chain can be excited by thermal fluctuations, including the motions of bond stretching, bond bending, torsion, etc. Torsion is the main source of polymer flexibility, and at room temperature its energy cost is about $k_B T$, where $T$ is the temperature and $k_B$ is Boltzmann’s constant. For a collection of a few adjacent monomers, the relative motions are usually small. But if the chain is very long, these motions can add up along the contour length (the maximum length of extension of the polymer), and reach a considerable amount, as depicted in Fig 1.1. As a result, polymer chains often appear flexible on length-scales rather larger than the size of an individual monomer. This flexibility is described by a “persistence length” $l_p$, beyond which the directional correlation of the polymer contour is lost. In our discussion of rubbery materials, the contour length of a polymer will be taken to be much longer than its persistence length, *i.e.*, $L \gg l_p$, and such polymers — flexible polymers — appear to be highly flexible, like a silk thread. In other

¹This acquisition of rigidity should not be confused with rigidity percolation, which captures the rigidity of athermal networks [12]. Here, in the case of soft random solids, the shear rigidity results from entropy of thermal fluctuations of the constituent particles, and is proportional to temperature.

²Strictly speaking, the name “gelation” has a broader meaning than vulcanization transition. It also includes the formation of chemical gels by adding random covalent bonds into systems of small molecules.
cases there are polymers with $L \ll l_p$, which are called stiff polymers.

![Figure 1.1: Local structure (left) and conformation of the whole chain (right) of a flexible polymer. Only the backbone atoms (denoted by black circles) are shown in the local structure. A long polymer chain with $L \gg l_p$ can be regarded as a flexible chain.](image)

Beyond the lengthscale $l_p$, we can model the polymer as being perfectly flexible, which means that all possible conformations of a polymer have equal energy. Therefore, the conformation of a polymer can be modeled as a non-selfavoiding random walk (ignoring excluded-volume interactions for the moment), which gives, via the central limit theorem, for the probability distribution for the end-to-end vector $\mathbf{R}$,

$$P_L(\mathbf{R}) = \left( \frac{d}{2\pi R_0^2} \right)^{d/2} e^{-\frac{d}{2R_0^2}||\mathbf{R}||^2}, \quad (1.1)$$

where $R_0 = \sqrt{Ll_p}$ and $L$ is the total contour length of the polymer. Therefore, one can characterize the size of the polymer using the root-mean-square end-to-end distance

$$\sqrt{\langle ||\mathbf{R}||^2 \rangle} = R_0 \propto L^{1/2}, \quad (1.2)$$

where the exponent 1/2 is the signature of the non-selfavoiding random walk model for the polymer chains. Such polymer chains, described by the non-selfavoiding random walk, are called ideal polymers. This exponent also indicates that the fractal dimension of ideal polymers is 2.

Applying the notions of microscopic statistical-mechanical ensembles, we know that the number of microscopic states $\Omega_L(\mathbf{R})$ consistent with a given end-to-end vector $\mathbf{R}$ is given by

$$\Omega_L(\mathbf{R}) \propto P_L(\mathbf{R}). \quad (1.3)$$
Thus, the entropy and the free energy of this state are given by

\[
S_L(\vec{R}) = k_B \ln \Omega_L(\vec{R}) = -\frac{k_B d |\vec{R}|^2}{2R_0^2} + \text{const}, \quad (1.4a)
\]

\[
F_L(\vec{R}) = -T S_L(\vec{R}) = \frac{k_B T d |\vec{R}|^2}{2R_0^2} + \text{const}. \quad (1.4b)
\]

Now imagine pulling this polymer by its two ends. The force \( f_L(\vec{R}) \) that one needs to exert in order to separate the two ends by \( \vec{R} \) is given by

\[
f_L(\vec{R}) = -\frac{\partial F_L(\vec{R})}{\partial \vec{R}} = -\frac{k_B T d}{R_0^2} \vec{R}. \quad (1.5)
\]

This is an entropic force, which tends to pull the two ends of a polymer together, as a result of the suppression (by separation) of the conformational fluctuations available to the polymer. In short, entropy “prefers” the two ends of a polymer to be near one another, so that more microscopic states (i.e., conformations) can be reached. From Eq. (1.5) we can see that this force is proportional to temperature \( T \). This is the signature of the entropic elasticity. This entropic force is actually the basic idea of the classical theory of rubber elasticity [6], as we shall discuss in Section 1.2.1.

More refined models of polymers take into account the fact that distinct monomers can not occupy the same region of space. To address this issue one can include a short-ranged repulsive interaction between pairs of monomers, which is called the excluded-volume interaction [13, 16, 17]. Thus, between any two monomers, either on the same polymer or on different polymers, in a solution or a melt, the potential energy of the excluded-volume interaction can be modeled as

\[
V_{\text{ex-vol}} = v \delta^{(d)}(\vec{R}_i(s) - \vec{R}_j(t)), \quad (1.6)
\]

where \( v \) is the excluded-volume parameter, which is in fact the second virial coefficient of the short-ranged repulsive interaction [16], and can understood as representing a small volume-element that is occupied by one monomer. Here, \( \vec{R}_i(s) \) stands for the position vector of the monomer at arclength \( s \) on polymer \( i \), and \( \vec{R}_j(t) \) for the position vector of the monomer at arclength \( t \) on polymer \( j \). The labeling of monomers using arclength are illustrated in Fig. 1.2.

The statistical physics of a polymer with excluded-volume interactions are described by the theory of “self-avoiding-walk” [13]. The scaling of the size of a polymer in the presence of excluded-volume interactions,

\[
\sqrt{\langle |\vec{R}|^2 \rangle} \propto L^\nu, \quad (1.7)
\]

was studied by Flory using a mean-field approximation [18] that gives \( \nu = 3/(d+2) \) (e.g., \( \nu = 0.6 \) in \( d = 3 \)). With renormalization-group theory and numerical
Figure 1.2: Illustration of arclength and the position vector of a polymer. The arclength $s$ is measured from a chosen end of the polymer, and it used as a coordinate system to label monomers, with $0 \leq s \leq L$. The position vector in space of the monomer at arclength $s$ is represented by $\vec{R}(s)$.

Simulations, the radius of gyration scaling exponent for the self-avoiding-walk universality class has been found for $d = 3$ to be

$$\nu \simeq 0.588.$$  \hspace{1cm} (1.8)

This excluded-volume interaction between monomers is also the reason for the incompressibility of rubber, as we shall see later.

1.1.3 The vulcanization transition

In 1839, Charles Goodyear (1800–1860) discovered the vulcanization process. He found that when natural rubber, a viscous liquid, is mixed with sulfur under heat, an elastic solid is formed. In this vulcanization process the sulfur particles act as crosslinkers to join together monomers on the polymers of natural rubber, as depicted in Fig. 1.1.3. The resulting vulcanized rubber overcomes many of the technological defects of natural rubber, such as permanent loss of shape after a deformation, and becoming sticky and easily deformed when warm, or brittle when cold. On the contrary, vulcanized rubber has remarkably stable elasticity (think of the tires of a car!), and returns remarkably accurately to its original shape when external stresses are released.

Early studies of gelation date back to the 1940s. The first quantitative theories of gelation—the mean-field theories — were proposed by Flory and Stockmayer [19, 20]. They modeled the gelation transition as a percolation transition on a Cayley tree [21].

The Cayley tree, as depicted in Fig. 1.4, can be built by starting with a central point (an “origin”) having $z$ (the coordination number) bonds emanating from it. Each bond leads to another site from which another $z$ bonds emanate. One of these $z$ bonds connects to the origin, and the other $z - 1$ bonds lead to new sites. This operation can be iterated to produce an infinite Cayley tree. The Cayley tree is a connected, cycle-free graph, and the infinite version of the Cayley tree, the Bethe lattice, is often used to develop mean-field theories [22].
Figure 1.3: Schematic of the vulcanization process. (a) Two polymers are joined when the crosslinker, denoted by the black dot, forms a covalent bond between the nearby monomers on these two polymers. (b) A network of crosslinked polymers.

To capture the gelation process, one can identify the sites on the Cayley tree as polymers and the bonds as crosslinks. In the crosslinking process, each bond has a certain probability $p$ to have been reacted (i.e., connected), so the corresponding bond in the Cayley tree is present with probability $p$ and absent with probability $1 - p$.

Consider the probability that the tree is connected, which means that there exists at least one path of bonds that connects the origin to infinity. Let us start from an arbitrary site (i.e., a “parent” site) that is already connected to the origin (the “grand ancestor”). The average number of additional bonds the “parent” forms with its $z - 1$ remaining neighbors (i.e., its “children”) is $p(z - 1)$. If this average number of bonds $p(z - 1)$ is less than unity, each new generation has, on average, fewer members, and the family can not survive for long. On the contrary, if this number $p(z - 1)$ is greater than unity, each generation has, on average, more members, and there forms an infinite cluster in the system. Therefore, the critical probability of linking, called the gel point $p_c$, is given by

$$p_c = \frac{1}{z - 1}.$$  \hspace{1cm} (1.9)

Other quantities of interest can also be found exactly in this model. For example, near the transition the gel fraction $Q$ (i.e., the fraction of sites that are members of the infinite cluster) grows linearly with $p - p_c$.

This classical theory of gelation happens to give a rather good estimate of the gelation threshold $p_c$. However, as a mean-field theory, it necessarily breaks down near the transition, in the sense of giving incorrect values for the various critical exponents.

A better model for the gelation process is the theory of percolation on a Euclidean lattice (for reviews see Refs. [21, 11, 23]). Percolation and its criticality have been analyzed using various tools, including the perturbative renormalization group via the Potts model [24, 25], conformal invariance (for $d = 2$) [26, 27], and numerical simulations [28, 29]. Nontrivial universality classes have been identified, revealing the rich physics of percolation.
1.2 Elasticity of soft random solids

1.2.1 Basics of rubber elasticity: classical theory

The most remarkable physical characteristic of rubbery material is the extraordinarily large reversible deformability, under the action of comparatively small stresses. A widely accepted theory explaining rubber elasticity is the classical theory of rubber elasticity, developed by Kuhn [31], Wall [32], Flory and Rehner [33], James and Guth [34], and Treloar [35]. The fundamental assumptions of the classical theory of rubber elasticity are (as summarized in Ref. [6])

1. The network contains \( n_c \) chains per unit volume, a chain being defined as the segment of polymer between successive crosslinks.

2. The root-mean-square end-to-end distance for the whole assembly of chains in the unstrained state is the same as for a corresponding set of free chains, and is given by Eq. (1.2).

3. There is no change of volume on deformation.

4. The crosslinks between chains move, on deformation, as if they were embedded in a homogeneous and isotropic elastic continuum (i.e., the affine deformation assumption).

5. The entropy of the network is the sum of the entropies of the individual chains, the latter being given by Eq. (1.4a).
Now consider the elastic free energy cost of a deformation that maps a mass point at \( \vec{r} \) to the new position \( \vec{R} \). This deformation can be expressed using the deformation gradient \( \Lambda_{ij}(\vec{r}) \equiv \partial \vec{R}_i(\vec{r})/\partial \vec{r}_j \). For a chain in the network with initial end-to-end distance \( \vec{r} \), from Assumption 4 we know that its end-to-end distance in the deformed state is given by

\[
\vec{R} = \Lambda \cdot \vec{r}.
\]  
(1.10)

(For simplicity we suppose that the deformation \( \Lambda \) is homogeneous.) Here, we use overhead arrows to denote vectors in \( d \)-dimensional space, such as \( \vec{r} \), and use bold letters to denote rank-2 tensors, such as \( \Lambda \). Using Eq. (1.4b), we have for the increase of the free energy of this polymer after deformation, which is its elastic free energy:

\[
F_{EL}^1 = k_B T d \left( |\vec{R}|^2 - |\vec{r}|^2 \right) = k_B T d \left( \Lambda^T \Lambda - I \right) \vec{r}.
\]  
(1.11)

Next, using Assumption 2, one argues that the total elastic free energy in unit volume \( F_{EL} \) is equivalent to the above single-chain elastic free energy \( F_{EL}^1 \), averaged over the distribution of initial end-to-end distances \( P_L(\vec{r}) \), and multiplied by the density of chains \( n_c \), which gives

\[
F_{EL} = n_c \langle F_{EL}^1 \rangle P_L(\vec{r}).
\]  
(1.12)

(For simplicity, we suppose that the contour length of each chain is \( L \).) With the distribution given in Eq. (1.1), we have \( \langle \vec{r}_i \vec{r}_j \rangle P_L(\vec{r}) = R_0^2 \delta_{ij}/d \), and thus we arrive at the free energy density

\[
F_{EL} = \frac{1}{2} n_c k_B T \text{Tr} (\Lambda^T \Lambda - I).
\]  
(1.13)

Assumption 3 introduces a constraint on the deformation that enforces incompressibility: \( \text{det } \Lambda = 1 \). This allows us to identify the coefficient \( n_c k_B T \) as the shear modulus \( \mu \) for the classical theory of rubber elasticity:

\[
\mu = n_c k_B T.
\]  
(1.14)

(See discussion in Chapter 4 for elucidation of this point.) Typical values of the shear modulus of rubber are in the range \( 10^4 - 10^6 \) Pa, which should be contrasted with typical bulk moduli of rubber, which are in the range \( \lambda \sim 10^9 - 10^{10} \) Pa. By contrast, conventional crystalline materials have bulk \textit{and} shear moduli in the range \( 10^{10} - 10^{13} \) Pa, values similar to those for the bulk (but not shear) modulus of rubber \cite{36}. Bulk moduli for both rubbery and crystalline materials originate in the energetic cost of atomic charge-cloud overlap, as do the shear moduli of crystalline materials. By contrast the shear moduli of rubbery materials are, as we have just discussed, entropic in origin.
1.2.2 Heterogeneity in the elasticity of soft random solids

The strongest assumption in the classical theory of rubber elasticity is likely to be the assumption of affine deformations (Assumption 4). It highly simplifies the real system into a mean-field model with single-chain statistics, and ignores thermal fluctuations of the crosslinks, interactions and quenched disorder.

In real rubber, firstly, the spatial locations of the crosslinks between polymers fluctuate thermally, as do the locations of other monomers, and these fluctuations contribute to the total elastic free energy, through phonon modes of wavelength greater than the typical mesh size in the network. Including these fluctuations is now known to modify the total elastic free energy in real rubber [37].

Secondly, there are strong excluded-volume interactions in real rubber. These are accounted for in a mean-field way via the incompressibility constraint \( \det \Lambda = 1 \) in the classical theory. In fact, this interaction has more profound effects via its interplay with thermal fluctuations [38, 37].

Thirdly, at the instant of crosslinking structural fluctuations are locked into the system, and thus the system has quenched fluctuations in its structure. Quenched fluctuation are fluctuations that are present for the lifetime of the sample’s existence, and can not be excited or relaxed thermally. In the language of statistical ensembles, quenched fluctuations are kept the same in each member of the ensemble of the system, as opposed to annealed fluctuations, which are excited thermally, and vary across the elements of the ensemble (in fact, defining the ensemble) [39]. These quenched fluctuations are a reflection of the thermal fluctuations in the liquid state. For example, some polymers, at the moment of crosslinking, might happen to be in a stretched state of higher free energy, while other polymers are in a lower free energy state. The crosslinking process, which can be modeled as instantaneous, locks in these thermal fluctuations, and the resulting state is necessarily heterogeneous. In particular, each monomer inhabits a unique spatial environment: some monomers are tightly constrained by crosslinks, and can move only over small regions of space, while other monomers are more loosely constrained, and explore larger volumes.

As a result, the structure of rubber is heterogeneous, and so is its elasticity. This means that the elastic parameters, such as the Lamé coefficients, can vary from place to place [40]. More interestingly, even in mechanical equilibrium there are large stresses present in the system, called residual stresses [41]. Physically, the Lamé coefficients are defined via the expansion of the elastic free energy \( F \) in terms of the strain tensor \( \epsilon_{ij} \):

\[
F = \frac{1}{2} \lambda (\text{Tr} \, \epsilon)^2 + \mu \text{Tr} \, \epsilon^2,
\]

where the parameter \( \lambda \) and \( \mu \) are called Lamé coefficients.

The elastic free energy can also be separated into two parts: hydrostatic compression (which changes the volume but retains the shape of the sample) and pure shear (which changes the shape but keeps the volume). In linear elasticity, which only linear order terms in the deformation vector \( \mathbf{u} \equiv \mathbf{R} - \mathbf{r} \) in the strain tensor \( \epsilon \) are kept, the elastic free energy can be...
nomenologically, this heterogeneous elasticity can also be viewed as quenched disorder, and can be modeled directly, in terms of an elastic free energy in which there are random elastic parameters, as we shall discuss in Chapter 4.

The statistics of the heterogeneous elasticity will be discussed in Chapters 3, 4, and 5.

1.3 Vulcanization theory

1.3.1 Basics of vulcanization theory

The main purpose of vulcanization theory is to provide a theoretical framework for the study of the criticality of the transition to the soft random solid state, and the consequent properties of the resulting soft random solid state, especially its elasticity. This approach is rooted in the pioneering work of Edwards and co-workers on the semi-microscopic formulation of the statistical mechanics of rubber [16], as well as the Edwards-Anderson theory of spin glasses [42]. These works provide the foundation and physical intuition for the development of the semi-microscopic theory, the Landau theory, and the renormalization-group theory of the vulcanization transition by Goldbart and co-workers, who investigated the criticality of the vulcanization transition, and also elasticity of the soft random solid state [43, 8, 44, 10].

In this section we shall discuss the Landau theory of the vulcanization transition, because it captures transparently the universality of the liquid-to-random solid phase transition and its pattern of spontaneous symmetry breaking. The corresponding semi-microscopic theory, which was actually developed earlier, and provided the foundations for the Landau theory, will be discussed in Chapter 3, in a simplified version.

The order parameter of the vulcanization transition is an unusual one. For the classical statistical mechanics of a many-particle system, one might naively be inclined to use the particle density as an order parameter. However, a simple particle density can not detect the transition between the liquid and the random solid state, because the disorder-averaged density is uniform (and has the same value) in both cases; a subtler order parameter is needed.

This order parameter, which is able to distinguish the liquid and the random solid state as, is constructed in the language of the replica method, which we now briefly review.

\[
F = \frac{1}{2}K(\text{Tr} \epsilon)^2 + \mu \text{Tr}(\epsilon - \frac{\text{Tr} \epsilon}{d} I)^2, \tag{1.16}
\]

where the first term describes hydrostatic compression, with the bulk modulus \( K = \lambda + 2d^{-1} \mu \), and the second term describes pure shear, with the shear modulus the same as the Lamé coefficient \( \mu \). For the case of rubber elasticity, because \( \mu \ll \lambda \) we shall not distinguish between \( K \) and \( \lambda \), and thus the two Lamé coefficients, \( \lambda \) and \( \mu \), are often referred to as the bulk modulus and shear modulus, respectively.
1.3.2 Brief review of the replica method

The first question to be asked before studying a system possessing quenched disorder is: what quantities ought to be averaged over the quenched disorder [45, 39, 46]?

For a system with a given configuration of the quenched variables (called a given realization of the disorder), the statistical mechanics is, in essentially all cases, impossible to study theoretically, because of the huge number of parameters involved and the absence of symmetry, moreover, the results are for a particular realization of disorder, and are not generally helpful. Thus, for a useful theoretical treatment of systems with quenched disorder, the description should be in terms of disorder-averaged quantities. But what are the quantities that should be disorder-averaged?

Loosely speaking, the answer is that one should generally average extensive variables. This has been illustrated by Brout [47]. Consider a very large system and divide it up into a large number of subsystems, such that each subsystem is macroscopic and clearly contains a distinct set of quenched random variables. Assume that interactions in the system are short-ranged, so that one can ignore the coupling between the subsystems. Thus, the value of any extensive variable for the whole system is the sum of this quantity over the subsystems. Given the large number of subsystems, the average over the subsystems is equivalent to an average over all possible choices of quenched disorder, according to a given, physically motivated, probability distribution for the quenched disorder.

Just as in ordinary statistical mechanics, where we know that the relative fluctuations of the energy around its thermal equilibrium are $O(N^{-1/2})$, we expect that the relative sample-to-sample fluctuations of the extensive also go to zero in the limit of large system. A quantity with this property is said to be self-averaging. For self-averaging quantities, not only can we expect the same results in experiments on different macroscopic samples, but we can also expect a theoretical calculation of the disorder average of the quantity to give the same answer as experiments would.

Therefore, the appropriate quantity to be averaged over is the free energy $F$, not the partition function $Z$. Moreover, an average of $Z$ is tantamount to treating quenched and annealed variables on the same footing, and thus would not reflect the equilibration of the annealed variables in the presence of a fixed background of quenched variables. We use the square brackets $\langle \cdots \rangle$ to denote disorder averages, so that the disorder-averaged free energy $\langle F \rangle$ is given by

$$
\langle F \rangle = \sum_x \mathcal{P}(\chi) F_\chi = k_B T \sum_x \mathcal{P}(\chi) \ln Z_\chi,
$$

where $\chi$ indexes the realizations of disorder, and $F_\chi$ is the free energy for a given realization $\chi$. The average over the realizations of disorder is weighted by some distribution of quenched disorder $\mathcal{P}(\chi)$, for which a model form has to be
determined.

The disorder average of the logarithm of the partition function \( \ln Z_\chi \) is very difficult to perform directly. There are, instead, various indirect mathematical tricks for doing this average, including the replica [48, 42], supersymmetry [49], and dynamical [50, 51] methods. For a comparison of these methods, see Ref. [52].

In vulcanization theory, it is the replica method that has primarily been utilized to deal with the disorder. In this section we briefly review the replica method. Its basis is the following mathematical identity

\[
x^n = e^{n \ln x} = 1 + n \ln x + O(n^2) \Rightarrow \ln x = \lim_{n \to 0} \frac{x^n - 1}{n},
\]  

(1.18)

which can be used to represent the logarithm in Eq. (1.17), so that one has

\[
[F] = k_B T \sum_\chi \mathcal{P}(\chi) \lim_{n \to 0} \frac{Z^n_\chi - 1}{n} = k_B T \lim_{n \to 0} \frac{[Z^n_\chi] - 1}{n}.
\]  

(1.19)

The essential problem is now to calculate the disorder average of \( Z^n_\chi \). Recall that each partition function \( Z_\chi = \text{Tr}_\{S\} e^{-\frac{H_\chi(\{S\})}{k_B T}} \) is a weighted sum over all possible microscopic states \( \{S\} \) in the statistical ensemble for the system. \( \{S\} \) might be the collection of conformations of the polymers or, in a magnetic system, the orientations of the spins.) Thus one can write

\[
Z^n_\chi = \text{Tr}_{\{S_1\}} e^{-\frac{H_\chi(\{S_1\})}{k_B T}} \text{Tr}_{\{S_2\}} e^{-\frac{H_\chi(\{S_2\})}{k_B T}} \cdots \text{Tr}_{\{S_n\}} e^{-\frac{H_\chi(\{S_n\})}{k_B T}}
\]  

\[= \text{Tr}_{\{S_1\}} \text{Tr}_{\{S_2\}} \cdots \text{Tr}_{\{S_n\}} e^{-\frac{1}{n} \sum \chi \{H_\chi(\{S_1\}) + H_\chi(\{S_2\}) + \ldots + H_\chi(\{S_n\})\},} \tag{1.20}
\]

One thus arrives at a formulation in which there are \( n \) thermodynamical systems, or statistical ensembles [but each with the same realization of disorder \( \chi \)]. They can also be understood as allowing for the description of \( n \) measurements on the system, each separated from the previous one by a very long time (certainly much longer than the correlation time of any microscopic dynamics). These ensembles are called the \( n \) replicas. They are evidently decoupled in Eq. (1.20). However, once one exchanges the order of the disorder average \( \cdots \) and the traces over all \( n \) replicas of the microscopic states \( \text{Tr}_{\{S_n\}} \), and carries out the disorder average, the replicas become coupled. This point will be discussed in more detail in the following sections, as well as in Chapters 3 and 4.

There have been criticisms of the replica method, mainly with respect to the analytical continuation of a theory with integer values of \( n \) to the \( n \to 0 \) limit. This limit seems to be risky in that none of the statistical systems in Eq. (1.20) survives. A discussion of this \( n \to 0 \) limit, and the related problem of the spontaneous breaking of replica symmetry, can be found in Refs. [45, 39, 46]. In vulcanization theory, we are primarily concerned with equilibrium statistical
mechanics at situations in which replica symmetry remains intact. We believe that the $n \to 0$ limit is less risky in this case.

Some simple but illuminating examples of the replica trick are given in Appendix A.

### 1.3.3 The order parameter of vulcanization theory

The appropriate order parameter for vulcanization theory should be able to distinguish the liquid state from the random solid state. As we have discussed in Section 1.3.1, a simple particle density cannot do the job, because the random solid state does not have the periodic density profile of a crystal. The essential difference between the liquid state and the random solid state can be described by *random particle localization*, i.e., the particles (which can be identified with either individual monomers or entire polymers) become localized in space in the random solid state, if they belong to the infinite cluster, while in liquid state their thermal fluctuations carry them throughout the whole space.

Inspired by the semi-microscopic theory of the vulcanization transition (see Chapter 3), the appropriate order parameter is a function $\Omega$ defined on $(1 + n)d$ dimensional replicated space:

$$
\Omega(\hat{x}) = \frac{1}{N} \sum_{j=1}^{N} \delta^{(d)}(x^0 - c^0_j) \delta^{(d)}(x^1 - c^1_j) \cdots \delta^{(d)}(x^n - c^n_j) \frac{1}{V_0 V^n},
$$

where $\hat{x} = (x^0, x^1, \ldots, x^n)$ is a position vector in $(1 + n)d$ dimensional replicated space. The replicas $1, \ldots, n$ correspond to the $n$ replicas as discussed in Section 1.3.2, and are called “measurement ensembles (or states”). The extra replica, 0, called the “preparation state”, arises from the Deam-Edwards distribution of the crosslinks (i.e., the model for the distribution of quenched disorder), and will be explained in Chapter 3. The vector $c^\alpha_j$ represents the position of particle $j$ (which can be understood as a monomer here\(^4\)) in replica $\alpha$. This order parameter measures the density function of a particle in each of the replicas, which are then multiplied together, followed by an average over the $N$ particles. The term $\frac{1}{V_0 V^n}$ is removed so as to ensure that the order parameter vanishes in the liquid state. Here, $V_0$ is the volume of the preparation ensemble (i.e., replica 0), and $V$ is the volume of the $n$ measurement ensembles (replicas 1, \ldots, $n$). The allowance for a change in volume is associated with a small contraction at the random-solidification transition, which will be discussed in detail in Chapter 3.

This order parameter is used to construct a field-theoretic description of the random solidification transition, in which a Landau free energy is proposed on symmetry grounds, as discussed in Section 1.3.4. Because each replica repre-

\(^4\)The particles can also be identified as polymers, as discussed in Chapter 3. The difference is merely one of microscopic details, and becomes unimportant when we look at large lengthscale physics, e.g., near the vulcanization transition.
sents a copy of the system having distinct thermal fluctuations, as discussed in Section 1.3.2, the average of this order parameter weighted by the Landau free energy corresponds to the following thermal- and disorder-averaged value of the order parameter:

\[
\langle \Omega(\hat{x}) \rangle_{H_\Omega} = \frac{1}{N} \sum_{j=1}^{N} \left[ \langle \delta^{(d)}(x^0 - c_j^0) \rangle_\chi \langle \delta^{(d)}(x^1 - c_j^1) \rangle_\chi \cdots \langle \delta^{(d)}(x^n - c_j^n) \rangle_\chi \right] - \frac{1}{V_0 V_n},
\]

(1.22)

where \( \langle \cdots \rangle_\chi \) represents a thermal average in a single copy of the system having a given realization of disorder \( \chi \), and each of these thermal averages corresponds to a distinct replica. This interpretation of the average order parameter is discussed in detail in Section 3.3.

In the liquid state, the particles are all delocalized, and thus one simply has \( \langle \delta^{(d)}(x^\alpha - c_j^\alpha) \rangle_\chi = 1/V_0 \) and \( \delta^{(d)}(x^\alpha - c_j^\alpha) \chi = 1/V \) (for \( 1 \leq \alpha \leq n \)). Thus \( \langle \Omega(\hat{x}) \rangle_{H_\Omega} = 0 \) in the liquid state.

In the random solid state, it is reasonable to hypothesize that the particles belonging to the infinite cluster are localized. Imagine that we measure the position of one localized particle, and then measure it again after a very long time. If the particle is delocalized, the two positions could each be anywhere in space and are uncorrelated. On the contrary, if the particle is localized, the two positions are both likely to be found near the mean position around which the particle fluctuates. In the language of the replica method, all replicas of the particle under consideration are likely to be found near a common but arbitrary spatial position.\(^5\) This is because, as we have discussed above, each replica corresponds to a copy of the same disordered system but with distinct thermal fluctuations, or measurements of the system separated by very long times. A particle localized as a part of the infinite cluster fluctuates around its fixed mean position, which is not changed by thermal fluctuations. Therefore, it is localized around the same mean position in each replica, thus the mean of the order parameter \( \langle \Omega(\hat{x}) \rangle_{H_\Omega} \) becomes nonzero and depends on the correlations of the densities between the distinct replicas.

From the above discussion, we see that the order parameter, Eq. (3.38), is able to distinguish between the liquid and the random solid state. A suitable form the this order parameter in the random solid state, and the pattern of spontaneous symmetry breaking associated with the liquid-to-random solid state phase transition, will be discussed in Section 1.3.4.

\(^5\)Strictly speaking, the localized infinite cluster can undergo global translations or rotations from replica to replica, and this corresponds to distinct equilibrium states of the field theory, connected by relative translations and/or rotations of the replicas.
1.3.4 Landau free energy and spontaneous symmetry breaking

The symmetry transformations of the vulcanization order parameter can be expressed explicitly in terms of a scalar field on \((1 + n)d\) dimensional space. These include translations of the replicas of space

\[
\hat{x} \rightarrow \hat{x}' = \hat{x} + \hat{a}, \\
\Omega(\hat{x}) \rightarrow \Omega'(\hat{x}') = \Omega(\hat{x}) = \Omega(\hat{x}' - \hat{a}),
\]

(1.23)

where \(\hat{a} \equiv (a^0, a^1, \ldots, a^n)\) represents a replicated translation. Similarly, under rotations of the replicas of space we have

\[
\hat{x} \rightarrow \hat{x}' = \hat{O} \cdot \hat{x}, \\
\Omega(\hat{x}) \rightarrow \Omega'(\hat{x}') = \Omega(\hat{x}) = \Omega(\hat{O}^{-1} \cdot \hat{x}'),
\]

(1.24)

where \(\hat{O} \equiv (O^0, O^1, \ldots, O^n)\) represents a replicated rotation.

The Landau free energy is constructed with the following two considerations:

- The Landau free energy has the full symmetry [Eqs. (1.23,1.24)], and so does the liquid-state order parameter. Due to random particle localization, the order parameter in the random solid state has broken symmetry for the relative translations and rotations between different replicas, but the symmetry of common translations and rotations of all replicas remains intact, reflecting the isotropy and homogeneity of the random solid state at the macroscopic level.

- The particle density in any \textit{single} replica is kept fixed, due to the strong excluded-volume interaction (corresponding to the incompressibility condition for rubber).

The first consideration is not hard to understand: as we have discussed in the previous section, the densities of a localized particle in different replicas are correlated (they appear near the same mean position in each replica/measurement); therefore, any relative translations and rotations would change the state. But the common translations and rotations of all replicas together is a preserved symmetry. On the contrary, the liquid state is homogeneous and isotropic, and is thus invariant not only for common but also for relative translations and rotations.
The second consideration puts a constraint on the order parameter:

\[ \frac{1}{N} \sum_{j=1}^{N} (\delta(d)(x^0 - c^0_j))_x = \frac{1}{V_0}, \]

\[ \frac{1}{N} \sum_{j=1}^{N} (\delta(d)(x^\alpha - c^\alpha_j))_x = \frac{1}{V} \quad \text{for } \alpha \geq 1, \]

\[ \Rightarrow \int \prod_{\beta(\neq \alpha) = 0}^n d^d x^\beta \Omega(\hat{x}) = 0 \quad \text{for all } \alpha. \quad (1.25) \]

This means that the single-replica density is uniform, because any density fluctuations are totally suppressed by the excluded-volume repulsion. Equation (1.25) is incorporated as a hard constraint on the field theory.

These considerations infer that the Landau free energy \( H \) can be written as

\[ H = \int d\hat{x} \left\{ \frac{T}{2} \Omega(\hat{x})^2 + \frac{1}{2} \sum_{\alpha=0}^{n} \left( \nabla^\alpha \Omega(\hat{x}) \right)^2 - \frac{v}{3!} \Omega(\hat{x})^3 \right\} \quad (1.26) \]

with the constraint Eq. (1.25). As in a typical Landau theory, at the classical level the phase transition occurs at \( r = 0 \). For \( r > 0 \) the liquid state is stable, and it becomes unstable at \( r < 0 \). This Landau free energy was originally derived from a semi-microscopic approach, as a leading-order expansion of the effective Hamiltonian; see Chapter 3 for details.

Incorporating the constraint Eq. (1.25) is perhaps clearer in momentum space. We define our Fourier transforms as

\[ \Omega_{\hat{p}} = \int d\hat{x} e^{-i\hat{p} \cdot \hat{x}} \Omega(\hat{x}), \]

\[ \Omega(\hat{x}) = \frac{1}{V_0 V^n} \sum_{\hat{p}} e^{i\hat{p} \cdot \hat{x}} \Omega_{\hat{p}}. \quad (1.27) \]

Then the constraint (1.25) translates to

\[ \Omega_{\hat{p}} |_{\hat{p}=0} = 1, \]

\[ \Omega_{p e^\alpha} = 0, \quad \text{for } p \neq 0, \quad (1.28) \]

where we have introduced a complete set of orthonormal basis vectors in replica space \( \{ e^\alpha \}_{\alpha=0}^n \), in terms of which any vector \( \hat{x} \) can be expressed as

\[ \hat{x} = \sum_{\alpha=0}^{n} x^\alpha e^\alpha, \quad (1.29) \]

where the coefficients \( x^\alpha \) are themselves, \( d \)-dimensional vectors. The condition \( \Omega_{p e^\alpha} = 0 \) (for \( p \neq 0 \)) is equivalent to Eq. (1.25). Because of this hard constraint of incompressibility, we shall separate the replicated space into a Lower Replica Sector (LRS), in which density fluctuations are completely suppressed [as in
Eq. (1.28)], and a Higher Replica Sector (HRS), which captures the correlations between distinct replicas, and has the instability at the liquid-to-random solid transition. The definitions of the LRS and HRS are (in momentum space) as follows: if a replicated momentum vector \( \hat{p} \equiv (p_0, p_1, \ldots, p_n) \) has either no or only one component \( p_\alpha \) being nonzero, and has all other components \( p_\beta = 0 \), then \( \hat{p} \in \text{LRS} \); on the other hand, if two or more components of \( \hat{p} \) are non-zero then we have \( \hat{p} \in \text{HRS} \).

Therefore, the only fields \( \Omega(\hat{x}) \) that feature in the Landau theory are the HRS ones (i.e., ones in which the Fourier amplitudes \( \Omega_{\hat{p}} \) are nonzero only for \( p \in \text{HRS} \)), and the LRS ones are completely constrained. In momentum space the Landau free energy then reads

\[
H = \sum_{\hat{p} \in \text{HRS}} \left( \frac{r}{2} + \frac{1}{2} |\hat{p}|^2 \right) \Omega_{\hat{p}} \Omega_{\hat{p}} - \frac{v}{3!} \sum_{\hat{p}_1, \hat{p}_2 \in \text{HRS}} \Omega_{\hat{p}_1} \Omega_{\hat{p}_2} \Omega_{\hat{p}_1 - \hat{p}_2}, \tag{1.30}
\]

(where for clarity we have omitted the \( \frac{1}{V_0 V_n} \) factors in each of the momentum summations). It is now apparent that the instability associated with the liquid-to-random solid transition at \( r > 0 \) happens only in the HRS. This indicates that the phase transition amounts to a change in the correlations among the distinct replicas.

The stationarity condition for the order parameter \( \Omega_{\hat{p}} \) is

\[
0 = \frac{\delta H}{\delta \Omega_{\hat{p}}} = (r + |\hat{p}|^2) \Omega_{\hat{p}} \Omega_{\hat{p}} - \frac{v}{2} \sum_{k \in \text{HRS}} \Omega_k \Omega_{\hat{p} - k}. \tag{1.31}
\]

It is evident that the liquid state \( \Omega_{\hat{p}} = 0 \) is always a solution to this stationarity point equation. From the form of free energy Eq. (1.30), we know that a new nonzero \( \Omega \) state will emerge for \( r < 0 \). The form of the order parameter (which has only an HRS part) in the random solid state is hypothesized to be

\[
\Omega_{\hat{p}} = Q \int \frac{dz}{V_0} \int d\tau \mathcal{P}(\tau) e^{-\frac{|z|^2}{2\tau}} e^{-i \sum_{n=1}^n p_\alpha (\xi \tau)} - Q \delta_{\hat{p}}^{(1+n)d}, \tag{1.32}
\]

which is parameterized by \( Q \) (i.e., the fraction of particles that are localized) and \( \mathcal{P}(\tau) \) (i.e., the distribution of inverse square localization lengths), where \( \tau \equiv 1/\xi^2 \) is the inverse square localization lengths, \( \xi \) is the localization length, and \( \delta_{\hat{p}}^{(1+n)d} \) is the Kronecker delta function in \((1+n)d\) dimensional momentum space. This form is probably easier to digest if we transform back to replicated real space, where it becomes

\[
\Omega(\hat{x}) = Q \int \frac{dz}{V_0} \int d\tau \mathcal{P}(\tau) \left( \frac{\tau}{2\pi} \right)^{(1+n)d/2} e^{-\frac{1}{\tau} \sum_{n=1}^n |x_\alpha^\tau - \xi z|^2} - \frac{Q}{V_0 V_n}. \tag{1.33}
\]

By comparing this form with the definition of the order parameter (1.21,3.38), one can understand the structure of this order parameter form. \( Q \) denotes the fraction of localized particles (i.e., the gel fraction). The density function of a
particle localized around a random position $\zeta z$ is given by $e^{-\frac{\tau}{2}|x^\alpha - \zeta|^2}$ in replica $\alpha$.  

Correspondingly, this particle was near position $z$ in the preparation state. The lengthscale of the thermal position fluctuations of a localized particle is characterized by a localization length $\xi$. Here, for historical reasons, we use the inverse squared localization length variable $\tau \equiv \frac{1}{\xi^2}$. Because the network is heterogeneous, each particle can have a widely different value of the localization length. This heterogeneity is characterized by the distribution $\mathcal{P}(\tau)$, which will be obtained by solving Eq. (1.31).

Inserting the hypothesized form (1.32) into the stationary condition (1.31), one gets the stationarity conditions on $Q$ and $\mathcal{P}(\tau)$. The resulting $Q$ is given by

$$Q = \frac{2|r|}{v},$$

(1.34)

for $r < 0$ (naturally, $Q = 0$ for $r \geq 0$); so near the transition, the fraction of localized particles grows linearly with the control parameter $|r|$.

The distribution of inverse squared localization lengths satisfies the integro-differential equation

$$\frac{\tau^2}{2} \frac{d\mathcal{P}(\tau)}{d\tau} = \left(\frac{\tau}{4} - \tau\right)\mathcal{P}(\tau) - \frac{|r|}{4} \int_0^\tau d\tau_1 \mathcal{P}(\tau_1)\mathcal{P}(\tau - \tau_1).$$

(1.35)

Figure 1.5: The universal function $\pi(t)$, which governs the scaling of the distribution $\mathcal{P}(\tau)$ of inverse square localization lengths.

This equation can be simplified by taking the scaling form

$$\mathcal{P}(\tau) = \frac{4}{|r|} \pi(t),$$

(1.36a)

$$\tau = \frac{|r|}{4} t.$$  

(1.36b)

$^6\zeta$ is a scalar parameter corresponding to a uniform contract of the whole volume due to crosslinking (see the discussion in Chapter 3).
One then finds that the universal function $\pi(t)$ obeys
\[
\frac{t^2 \, d\pi(t)}{2 \, dt} = (1 - t)\pi(t) - \int_0^t dt' \pi(t')\pi(t - t').
\] (1.37)

Combining with the normalization condition $\int_0^\infty dt \pi(t) = 1$, the asymptotic forms of $\pi$, valid for small and large $t$, can be derived analytically, and have proven to give a quite accurate solution to Eq. (1.37); see Refs. [8, 43] for details. The fundamental conclusion is that the function $\pi(t)$ has a peak at $t \approx 1$ of width of order unity, and decays rapidly both as $t \to 0$ and as $t \to \infty$, as shown in Fig. 1.5. By combining these features of $\pi(t)$ with the scaling form, Eq. (1.36), we see that the typical inverse squared localization length scales as $|r|$ [see Eq. (1.36b)], and thus the typical localization length $\xi$ scales as $|r|^{-1/2}$ near the transition to the random solid state.

1.3.5 Applications of vulcanization theory

Vulcanization theory captures the basic pattern of symmetry breaking at the liquid-to-random solid phase transition. This pattern of symmetry breaking and the concept of particle localization have universal meaning in the general case of random solidification transitions, without reference to any microscopic details, and is not peculiar to randomly crosslinked polymer systems.

The renormalization-group analysis of this vulcanization theory has been carried out by Peng and Goldbart [10], and subsequently by Peng et al. [53] and Janssen and Stenull [54]. A $6 - \epsilon$ expansion is studied, yielding a nontrivial fixed-point and critical exponents that are consistent with percolation theory, but with additional characterization of the thermal fluctuations.

Along these lines, a renormalization-group analysis of the emergence of entropic shear rigidity at the vulcanization transition was studied by Xing et al. [38]. In this setting, two universality classes were identified and analyzed, corresponding to phantom elastic networks and dense systems possessing strong excluded-volume interactions, respectively.

The Goldstone fluctuations in the random solid phase have also been investigated by Mukhopadhyay et al. [55], and by Goldbart et al. [56]. These Goldstone fluctuations have been identified with shear deformations, and their properties have been explored.

Vulcanization theory has also been extended and applied to the elasticity of liquid crystal elastomers [57], and to glassy correlations and micro-phase-separation in crosslinked homopolymer blends [58], semiflexible polymers [59], etc., revealing a rich spectrum of physics that can be investigated via this framework.

In Chapters 3, 4, and 5, we shall study the heterogeneity of the elastic properties of soft random solids, via an approach that involves identifying the Goldstone fluctuations, and constructing an interpretation of the Goldstone
theory in terms of a phenomenological model of a quenched random elastic medium.

1.4 Basics of Goldstone fluctuations

1.4.1 Spontaneous breaking of continuous symmetries

Spontaneous Symmetry Breaking (SSB) is one of the most important concepts in modern physics. It takes place when a system whose Hamiltonian and equilibrium state are symmetric with respect to some symmetry group makes a transition to an equilibrium state that is less symmetric. The free energy of the system has the full symmetry but, by tuning the parameters, the states with the lowest free energy can become a set of states that break the full symmetry.

This can be illustrated using the mean-field $xy$ [also called $O(2)$ vector] model. The order parameter of the $xy$ model is a two-component vector, and can be parameterized as $\psi = s(\cos \theta, \sin \theta)$. The symmetry transformation of this order parameter is $\psi \rightarrow \psi' = O\psi$, where $O$ is a rank-2 orthogonal matrix. Orthogonality requires that $O^T = O$, and so $|\psi|^2$ is invariant with respect to this transformation.

The free energy is invariant with respect to this $O(2)$ transformation of the order parameter, and so the Landau theory is, retaining just the few lowest order terms,

$$F = \int d^d x \left\{ \frac{r}{2} |\psi|^2 + \frac{1}{2} |\nabla \psi|^2 + \frac{u}{4!} (|\psi|^2)^2 \right\},$$

(1.38)

where $\nabla$ denotes spatial derivatives, and $|\nabla \psi|^2 \equiv \sum_{j=1}^d \partial_j \psi \partial_j \psi$.

The equilibrium state of this free energy should be homogeneous in space, so that the $|\nabla \psi|^2$ is minimized. As a result, the problem simplifies to one of a free energy of a spatially independent order parameter $\psi$:

$$f = \frac{r}{2} |\psi|^2 + \frac{u}{4!} (|\psi|^2)^2.$$  

(1.39)

This free energy has qualitatively different structures for $r > 0$ and $r < 0$ (assuming $u > 0$), as illustrated in Fig. 1.6. For $r > 0$, the minimum of the free energy is at $\psi = 0$, which preserves the $O(2)$ symmetry. On the other hand, for $r < 0$ the minimum is on the circle with $|\psi|^2 = s_0^2 = \frac{u|s|}{r}$. The equilibrium state of the system, in the thermodynamic limit, can only choose one point on this circle [60], with an arbitrary value of $\theta$, and thus the $O(2)$ symmetry is spontaneously broken.

1.4.2 Goldstone modes and generalized elasticity

In the case of SSB in the $xy$ model, the broken symmetry $O(2)$ is a continuous symmetry. In the language of particle physics, Goldstone’s theorem states that
whenever a continuous symmetry is spontaneously broken, new *massless* scalar particles appear in the spectrum of possible excitations. There is one scalar particle — called a Goldstone boson — for each generator of the symmetry that is broken, *i.e.*, that is not preserved in the equilibrium state [61, 62].

In the example of $xy$ model, the broken $O(2)$ symmetry gives exactly one Goldstone boson. For example, we may choose the equilibrium state to be $\psi_0 = (s_0, 0)$, which means $\theta = 0$, as shown in Fig. 1.7. Obviously, this state breaks the $O(2)$ symmetry. In fact, a symmetry operation $O$ will move this state to another equilibrium state on the circle.

With fluctuations around the ground state $\psi_0$, we can write the order parameter as $\psi(x) = \psi_0 + \delta\psi(x)$, which can be parameterized via $\delta s(x)$ and $\delta\theta(x)$ (note that the fluctuations can vary in space) as:

$$\psi(x) = (s_0 + \delta s(x))(\cos\delta\theta(x), \sin\delta\theta(x)).$$

Inserting this order parameter into the free energy Eq. (1.38), and using $s_0^2 = \frac{6|r|}{\nu}$, we find that

$$F = F_0 + \int d^d x \left\{ \frac{|r|}{2} |\delta s(x)|^2 + \frac{1}{2} |\nabla \delta s(x)|^2 + \frac{1}{2} s_0^2 |\nabla \delta\theta(x)|^2 \right\}. \quad (1.41)$$

It is evident that the field $\delta s(x)$ has mass $|r|$, but the $\delta\theta(x)$ field is massless. Low-energy excitations do not touch $\delta s(x)$, so the low-energy version of the theory will be (dropping the unimportant constant equilibrium state energy part) is given by

$$F = \frac{1}{2} \rho_0 \int d^dx |\nabla \delta\theta(x)|^2, \quad (1.42)$$

---

7In the language of condensed matter physics, “particles” here should be associated with modes of fluctuations of the system, and “mass” with the inverse of susceptibility (*i.e.*, coefficient of the the quadratic term in free energy).

---

Figure 1.6: The potential of the $xy$ model: (a) for $r > 0$; and (b) for $r < 0$. 
with the stiffness of the Goldstone mode $\rho_\theta$ is given by

$$\rho_\theta = s_0^2 = \frac{6|\mathbf{r}|}{u}. \quad (1.43)$$

Figure 1.7: Fluctuations around the ground state $\psi_0$ in the broken symmetry phase of the $xy$ model. The fluctuation $\delta \psi$ consists two sectors, a massive sector, $\delta s$, in which the potential increases quadratically with $|\delta s|$; and the massless Goldstone sector, $\delta \theta$, which is along the “valley” of the potential energy.

The Goldstone mode $\delta \theta(x)$ is massless in this state, and the energy-cost of its spatial variations is characterized by $\rho_\theta$. A typical spatial configuration of a low energy Goldstone type fluctuation is depicted in Fig. 1.8.

Figure 1.8: A typical spatial configuration of a low-energy Goldstone mode. The arrows represent the local directions of the $\psi$ field.

From this example we see that, for theories possessing Goldstone modes, a global change of the value of the order parameter cost no energy, and only the
distortions of the state in space do cost energy. This is similar to the elastic free energy, in which displacements of the whole elastic medium do not cost energy, but relative displacements do. In fact, this free energy associated with the spatial distortion of the Goldstone mode, is called the generalized elasticity [36].
Chapter 2

Cavity approach to the random solid state

In vulcanization theory, the mean-field equilibrium state of soft random solids is specified by two diagnostics: the fraction of localized particles $Q$ and the distribution of localization lengths (or more usefully, the inverse squared localization lengths) $\mathcal{P}(\tau)$. Simple equations for $Q$ and $\mathcal{P}(\tau)$, Eqs. (1.34) and (1.35), follow from the stationarity of the mean-field free energy with respect to the order parameter $\Omega$. [Actually, a more precise equation for $Q$, valid not just near the phase transition but, rather, for any value of the density of links, is given by the semi-microscopic model; see Eq. (3.43).] This simplicity suggests that one should be able to establish a heuristic and physically transparent method, valid at least at the mean-field level, for characterizing the liquid-to-soft random solid transition that avoids the powerful but strange mathematical subtleties of the replica approach.

Such an approach can be established via the cavity method [39, 63] (which is similar to the Thouless-Anderson-Palmer (TAP) approach [64]). The cavity method has proven flexible and powerful in the analysis of a variety of other disordered systems, e.g., spin glasses. The present work is based on the version used to address spin glasses having finite connectivity [63].

In this chapter, we review our cavity approach to soft random solids [65]. It is worth mentioning that we view the cavity method as complementing rather than supplanting the replica method: the latter provides access to the powerful array of field-theoretic tools beyond mean field.

2.1 Cavity method for crosslinked polymer networks: vulcanization transition region

We begin by considering a system of vulcanized polymers, as depicted in Fig. 2.1 a. We characterize the system by the fraction of localized particles $Q$, and the statistical distribution $\mathcal{N}$ of the squared localization lengths $\xi^2$ of the localized particles. Here, we follow the notations in Ref. [65], and use the distribution of squared localization lengths $\mathcal{N}(\xi^2)$, rather than the distribution of inverse squared localization lengths $\mathcal{P}(\tau)$ (where $\tau \equiv 1/\xi^2$). The relationship between the two descriptions will be summarized in the results; see Eq. (2.18).
Figure 2.1: (a) Snapshot of a crosslinked (open circles) polymer system, in which a fraction $Q$ of the polymers belong to the infinite cluster (and are thus localized), and the remaining fraction $1-Q$ are delocalized. A localized segment exhibits thermal position-fluctuations over a length-scale $\xi$ (i.e., its localization length). Due to the heterogeneity of the network, distinct segments have distinct localization lengths. (b) Coupling of a new polymer (dashed) to the system in order to probe the distribution $N(\xi^2)$. The new polymer has $N_c$ contact points with the existing network, and crosslinks are introduced independently at these points.

The first step is to envisage adding a further polymer to the system, as shown in Fig. 2.1 b. Of all the segments on this chain, \(^1\) we suppose that a certain number $N_c$ are sufficiently close to segments of the original system to have a chance of becoming crosslinked to them. We suppose that fluctuations in this number are sufficiently small that we may neglect them. Next, we consider a random crosslinking process that results, with independent probability $p$, in crosslinks actually being introduced between each of the $N_c$ close pairs. Within this framework, the probability that exactly $k'$ crosslinks are introduced is then given by the binomial formula

$$
\binom{N_c}{k'} p^{k'} (1-p)^{N_c-k'}.
$$

We now ask the question: What is the probability $\mathcal{P}_k$ that exactly $k$ of these crosslinks are made to localized segments? To answer it, we make the approximation that whether or not the segments of the original system are localized are independent random events. We refer to the probability of any one such segment being localized as $Q$. Then, collecting together the contributions to this probability, which arise from $k'$ ($k \leq k' \leq N_c$) crosslinks being formed, of which exactly $k$ are to localized segments, we arrive at the formula

$$
\mathcal{P}_k = \sum_{k'=k}^{N_c} \binom{N_c}{k'} p^{k'} (1-p)^{N_c-k'} \binom{k'}{k} Q^k (1-Q)^{k'-k}.
$$

\(^1\)The concept of “segments” refer to portions on a polymer having lengths of order the persistence length $l_p$, which enable one to view the polymer as freely-joined segments.
Via a straightforward application of the binomial theorem one can perform this summation, and hence arrive at the result

\[ \mathcal{P}_k = \binom{N_c}{k} (pQ)^k (1-pQ)^{N_c-k}. \]  

(2.3)

Let us evaluate these probabilities for the three cases of relevance, viz.,

\[ \mathcal{P}_0 = (1-pQ)^{N_c}, \]  

(2.4a)

\[ \mathcal{P}_1 = N_c pQ (1-pQ)^{N_c - 1}, \]  

(2.4b)

\[ \mathcal{P}_2 = \frac{1}{2} N_c (N_c - 1) (pQ)^2 (1-pQ)^{N_c - 2}. \]  

(2.4c)

Near the transition, which is the regime of prime interest, we have \( Q \ll 1 \). We also assume that \( p \ll 1 \) and \( N_c \gg 1 \), but \( N_c p \) is finite, indicating that the mean number of crosslinks formed (to either delocalized polymers or localized polymers in the infinite cluster) is finite, so \( pQ \ll N_c pQ \ll 1 \); then these probabilities simplify to

\[ \mathcal{P}_0 \approx e^{-N_c pQ}, \]  

(2.5a)

\[ \mathcal{P}_1 \approx e^{-N_c pQ} N_c pQ, \]  

(2.5b)

\[ \mathcal{P}_2 \approx e^{-N_c pQ} \frac{1}{2} N_c (N_c - 1) (pQ)^2. \]  

(2.5c)

To arrive at a self-consistent equation for \( Q \) (as a function of \( p \) and \( N_c \)) we require that the probability of the added polymer being crosslinked to exactly zero localized segments be \( 1-Q \), which gives

\[ 1 - Q = (1-pQ)^{N_c}. \]  

(2.6)

In the limit \( pQ \ll 1 \) this becomes

\[ 1 - Q = e^{-N_c pQ}. \]  

(2.7)

For \( N_c p < 1 \), this equation has only one solution: \( Q = 0 \), representing the liquid state; but for \( N_c p \geq 1 \) another solution emerges, in addition to \( Q = 0 \), as shown in Fig. 2.2, representing the random solid state, which has a finite fraction of particles being localized, and is the stable state for \( N_c p \geq 1 \).

By identifying that \( N_c p \equiv \eta^2 \) is actually the mean coordination number (i.e., mean number of crosslinks made to one polymer; see the discussion in Section 3.1), we see that we have arrived at precisely the equation for \( Q \) that was obtained via the semi-microscopic theory and the replica method. The same equation has been found by Erdős and Rényi in their classical work on the statistical properties of random graphs [66]. This relation between \( Q \) and \( \eta^2 \) is not restricted to the transition region, but Eq. (1.34) is, and it can be seen as a leading-order expansion of Eq. (2.7). Of course, they are both mean-field
relations, and the scaling of the fraction of the localized particles very near the critical point would only be given correctly by a renormalization-group (or other, more accurate) analysis, as in Ref. [10].

The second step is to arrive at a self-consistent equation for \( N(\xi^2) \) (as a function of \( p, N_c \), and \( \xi^2 \)). To achieve this we address the probability that the segment at arclength \( \sigma \) on the added polymer has squared localization length \( \xi^2 \). The arclength \( \sigma \) (1 \( \leq \sigma \leq 1 \)) measures the distance of the segment from a particular end of the polymer, as a fraction of the total arclength.

As the segments of the added polymer will only be localized if they are attached to at least one localized segment of the original system, we should replace the probabilities \( P_k \) by the probabilities conditioned on at least one crosslink being made to the localized cluster. Thus, we have the conditional probabilities (for \( k \geq 1 \)):

\[
\hat{P}_k = \frac{P_k}{1 - P_0}.
\]

(2.8)

In particular, we are interested in two cases: the polymer being linked with one segment to the localized cluster \( \hat{P}_1 \), or being linked with two segments to the localized cluster \( \hat{P}_2 \). With the assumption that \( pQ \ll 1 \), we know that \( \hat{P}_1 \gg \hat{P}_2 \gg \hat{P}_3 \cdots \), so we only keep the first two orders and put \( \hat{P}_1 = 1 - a \) and \( \hat{P}_2 = a \), where \( a \) is a small parameter, \( O(N_c p Q) \).

Consider the case in which the added polymer is crosslinked at its arclength \( \sigma_1 \) to a \textit{single} segment of the original system, and let the squared localization length of that segment in the original system be \( \xi_1^2 \), as depicted in Fig. 2.1 a. Furthermore, suppose that the added chain has Gaussian statistics. Then, by the elementary properties of random walks, the mean-square spatial separation of segments separated by arclength \( |\sigma - \sigma_1| \) is given by \( |\sigma - \sigma_1| R_g^2 \), where \( R_g^2 \) is the mean squared end-to-end distance of each chain. Thus, if \( \mathcal{N} \) is the distribution for the squared localization length of the segment of the original system, to which the new chain is crosslinked at arclength \( \sigma_1 \), the distribution of the square

---

Figure 2.2: Stable solution of the self-consistency equation for the fraction of localized particles \( Q \).
localization length \( \xi^2 \) for the segment at arclength \( \sigma \) on the new chain will be given by

\[
\int d\xi_1^2 N(\xi_1^2) \delta(\xi^2 - (\xi_1^2 + |\sigma - \sigma_1|R_g^2)) = N(\xi^2 - |\sigma - \sigma_1|R_g^2).
\] (2.9)

Now, supposing that the addition to the squared localization length, \( |\sigma - \sigma_1|R_g^2 \), is small compared with the squared localization lengths that feature with appreciable weight in \( N(\xi^2) \), \textit{i.e.}, the size of the polymer is much smaller than the typical localization length, Eq. (2.9) approximates to

\[
N(\xi^2 - |\sigma - \sigma_1|R_g^2) \approx N(\xi^2) - |\sigma - \sigma_1|R_g^2 N'(\xi^2).
\] (2.10)

![Figure 2.3](image)

Figure 2.3: (a) The added polymer is attached at a single segment to the infinite cluster (\textit{i.e.}, the shaded region). (b) The added polymer is attached at two segments to the infinite cluster.

Next, consider the situation in which the added polymer is crosslinked at its pair of arclengths \( \sigma_1 \) and \( \sigma_2 \) to \textit{two} segments of the original system, these segments having respectively squared localization lengths \( \xi_1^2 \) and \( \xi_2^2 \), as shown in Fig. 2.1 b. In fact, as the probability that the added chain has two crosslinks to localized segments of the original system is (in the limit of interest) much smaller than the probability that it has one crosslink, we shall not need to keep track of the arclength locations of the crosslinks; in this situation it will be adequate to treat the added chain as a point object. Then, as this object is attached to \textit{two} localized objects, it is pinned more sharply than either of them, this \textit{parallel} form of pinning giving rise to a smaller square localization length \( \xi^2 \), via the formula

\[
\xi^{-2} = \xi_1^{-2} + \xi_2^{-2}.
\] (2.11)

So, assuming that \( \xi_1^2 \) and \( \xi_2^2 \) are \textit{independent} \textit{[and thus governed by the joint}
distribution \(N(\xi_1^2)N(\xi_1^2))\), the resulting distribution of \(\xi^2\) is given by

\[
\int d\xi_1^2 N(\xi_1^2) \int d\xi_2^2 N(\xi_2^2) \delta(\xi^2 - (\xi_1^{-2} + \xi_2^{-2})^{-1}).
\]  

(2.12)

We now put these results together to construct the distribution of squared localization length for segment \(\sigma\) of the added chain, arriving at the consistency equation of the distribution of square localization lengths:

\[
N(\xi^2) = (1 - a)(N(\xi^2) - |\sigma - \sigma_1|\mathcal{R}_g^2 N'(\xi^2)) \\
+ a \int d\xi_1^2 N(\xi_1^2) \int d\xi_2^2 N(\xi_2^2) \delta(\xi^2 - (\xi_1^{-2} + \xi_2^{-2})^{-1}).
\]  

(2.13)

Finally, we average over the segment \(\sigma\) of the added chain, as well as the location \(\sigma_1\) of the crosslink, using

\[
\int d\sigma \int d\sigma_1 |\sigma - \sigma_1| = \frac{1}{3},
\]  

(2.14)

thus arriving at the self-consistent equation obeyed by the distribution of squared localization lengths:

\[
N(\xi^2) = (1 - a)(N(\xi^2) - \frac{1}{3} \mathcal{R}_g^2 N'(\xi^2)) \\
+ a \int d\xi_1^2 N(\xi_1^2) \int d\xi_2^2 N(\xi_2^2) \delta(\xi^2 - (\xi_1^{-2} + \xi_2^{-2})^{-1}).
\]  

(2.15)

Observe that by integrating both sides over \(\xi^2\), and invoking the property that \(N(\xi^2)\) vanishes in the limits \(\xi^2 = 0\) and \(\xi^2 \to \infty\), we recover the normalization condition that \(\int d\xi^2 N(\xi^2) = 1\).

The scaling property of \(N(\xi^2)\) shows up via the following change of dependent and independent variables:

\[
\xi^2 \rightarrow t \equiv \frac{2}{3} a \frac{\mathcal{R}_g^2}{\xi^2},
\]  

(2.16a)

\[
N(\xi^2) \rightarrow \pi(t) \equiv \frac{3}{2} \frac{a}{1 - a} \frac{\xi^2}{\mathcal{R}_g^2} N(\xi^2),
\]  

(2.16b)

under which Eq. (2.15) becomes

\[
\frac{t^2}{2} \frac{d\pi(t)}{dt} = (1 - t)\pi(t) - \int_0^t dt' \pi(t') \pi(t - t').
\]  

(2.17)

This is precisely Eq. (1.37). Comparing the scaling in Eq. (2.16) and (1.36), we identify that the parameter \(|r|\) in the Landau theory corresponds to \(\frac{6a}{(1-a)\mathcal{R}_g^2}\) (to leading order in \(pQ\)).

In addition, the relation between the distribution of the squared localization
lengths and the inverse square localization lengths is given by

$$N(\xi^2) = \tau^2 P(\tau).$$  \hspace{1cm} (2.18)

Notice that the cavity method allows us to compute corrections to Eq. (2.17) perturbatively in $1/R_g^2$.

### 2.2 Cavity method for the randomly linked particle model: arbitrary link-densities

The cavity approach can be extended to a simpler model network. Consider a system composed of $N$ point-like particles undergoing Brownian motion at a certain temperature $T$. A liquid-to-random solid transition can be triggered by introducing random covalent bonds between particles that are nearby in the liquid state. This model can capture the essence of the chemical gelation transition and, in fact, in a coarse grained view it also characterizes the vulcanization transition exhibited by long flexible polymers; see the detailed discussion in Chapter 3. We shall call this model the Randomly Linked Particle Model (RLPM); see Refs. [65, 67, 68, 69].

In the RLPM, the random covalent bonds are modeled as springs of zero-rest-length (see the discussion of this assumption in Section 3.1). Thus, the probability distribution $\phi$ of the separation of the two particles linked by this bond $\vec{c}_i - \vec{c}_j$ is Gaussian and characterized by a length-scale $b$ (which scales with temperature as $b \sim T^{1/2}$):

$$\phi(\vec{c}_i - \vec{c}_j) \propto e^{-\frac{|\vec{c}_i - \vec{c}_j|^2}{2b^2}},$$ \hspace{1cm} (2.19)

where $\vec{c}_i$ and $\vec{c}_j$ are the position vectors of particles $i$ and $j$. This model is sufficiently simple that the analysis of it need not be restricted to the critical region and can be extended to any density of links.

To approach the statistics of the RLPM using the cavity method, we consider the process of adding a new particle. The combinatorics of the bonding follows the form taken for the system of crosslinked polymers; we simply need to convert the notion of contact points into spherical regions of a certain radius in which the likelihood of particles being bonded to one another is concentrated. This sphere is centered on the new particle and, on average, includes $N_c$ of the existing particles. Then, bonds are randomly introduced, with probability $p$, between the new particle and some of the $N_c$ existing particles that are nearby. Thus, the foregoing combinatorics continues to apply, and we arrive at the formula for the probability of having exactly $k$ bonds with the infinite cluster given in Eq. (2.3). As a consequence, we obtain the foregoing result for the fraction of the infinite cluster $Q$, Eq. (2.7).

The physics of the localization length is, in fact, simpler for the RLPM. When
the new particle is connected via a spring of length \( b \) to \( one \) localized particle, its localization length \( \Xi_1 \) is given by \( \Xi_1 = (\xi_1^2 + b^2) \). When it is connected in \( parallel \) via identical springs to \( k \) localized particles, its localization length \( \Xi_k \) is given by

\[
\frac{1}{\Xi_k} = \sum_{j=1}^{k} \frac{1}{\xi_j^2 + b^2}.
\]  

(2.20)

To construct the distribution of the square localization length of the new particle, we shall average over all possible numbers of bonds, weighted by their corresponding probabilities. These probabilities follow from the probabilities \( P_k \) given by Eq. (2.3), but normalized by a factor \( Q^{-1} \) because the new particle will only be localized if it is bonded to at least one particle in the infinite cluster. Hence, we arrive at a self-consistency equation for SLL distribution for the RLPM:

\[
N(\xi^2) = \sum_{k=1}^{\infty} \hat{P}_k \int d\xi_1^2 N(\xi_1^2) \cdots d\xi_k^2 N(\xi_k^2) \delta(\xi^2 - \Xi_k^2),
\]

(2.21)

where the conditional probabilities \( \hat{P} \) are given by \( \hat{P} = P/Q \) (for \( k = 1, 2, 3, \ldots \)).

The distribution of squared localization lengths for the RLPM was obtained previously by Broderix \( et al. \) \cite{69} using the replica method and a Mayer expansion. To see that the cavity approach result, Eq. (2.21), recovers their result, we take the limit \( N_c \to \infty \) while keeping finite the mean number of bonds from the new particle (either to the infinite cluster or to delocalized particles), \( i.e., pN_c \). In this limit, the binomial distribution tends to a Poisson distribution:

\[
\hat{P}_k \to \left( \frac{(pN_c)^k Q^{k-1}}{k!} e^{-pN_c Q} \right).
\]

(2.22)

The result of Broderix \( et al. \) \cite{69} then follows from Eq. (2.21) by (i) transforming to a distribution for the inverse squared localization lengths \( \tau \equiv 1/\xi^2 \), and (ii) making the identifications \( \kappa = b^{-2} \) and \( c = pN_c \) (\( i.e., \) the mean of coordination number).
Chapter 3

The semi-microscopic approach: the randomly linked particle model

The randomly linked particle model (or RLPM) is a convenient minimal model of soft random solids, inasmuch as it adequately captures the necessary long-wavelength physics. It can be viewed as a simplified version of the vulcanization theory [43, 56], with the microscopic details, such as the polymer chain conformations, being ignored. Nevertheless, it is able to reproduce the same universality class as vulcanization theory at the liquid-to-random solid transition. For the study of elasticity, we shall consider lengthscales on which the system is a well-defined solid (i.e., scales beyond the “localization length”, as we shall see later in this Thesis). These lengthscales are much larger than the characteristic linear dimension of an individual polymer.

3.1 The model

The RLPM consists of \( N \) particles in a volume \( V \). In order to study the elasticity, including bulk deformations, this volume \( V \) is allowed to fluctuate under a given pressure \( p \). The positions of these particles in this fluctuating volume are denoted by \( \{c_j\}_{j=1}^N \). The particles in the RLPM interact via two types of interactions: the excluded volume interaction between any two particles (either direct or mediated by a solvent) [13, 16, 17], and the attractive interactions between the particles that have randomly been chosen to be linked. Thus, the Hamiltonian can be written as

\[
H_\chi = \frac{\nu^2}{2} \sum_{i,j=1}^N \delta(c_i - c_j) + \sum_{e=1}^M v_L |c_{i_e} - c_{j_e}|. \tag{3.1}
\]

Here, the label \( e \) indexes the links in a given realization of the quenched disorder, from 1 to the total number of links \( M \). Between each pair that is being linked there is an attractive potential energy \( v_L \), which we term a soft link (as opposed to the usual hard constraints of vulcanization theory).

The particles of the RLPM can be identified with coarse-grained polymers or small molecules, and the soft links, can be identified with Gaussian molecular chains or covalent bonds that bind the small molecules to one another. For
Gaussian chains, the potential can be modeled as

\[ v^{(GC)}_L(|r|) = \frac{k_B T |r|^2}{2a^2}, \]  

(3.2)

i.e., a harmonic attraction, or a “zero rest-length” spring, of lengthscale \( a \) between the two particles. In making this coarse-graining one is assuming that microscopic details (e.g., the precise locations of the crosslinks on the polymers, the internal conformational degrees of freedom of the polymers, and the effects of entanglement) do not play significant roles for the long-wavelength physics. In part, these assumptions are justified by studying more detailed models, in which the conformational degrees of freedom of the polymers are retained [8].

For chemical gels, the links are covalent bonds, and can be modeled as

\[ v^{(CB)}_L(|r|) = k \left(|r| - l\right)^2, \]  

(3.3)

i.e., as springs of rest-length \( l \), representing the (mechanical) equilibrium length of the bond.

In the following discussion, we shall use the Gaussian chain potential, Eq. (3.2) for simplicity. For the long-wavelength physics, the difference between these two potentials is a microscopic detail and can be ignored [see the discussion below Eq. (3.34)].

From the discussion above, the RLPM can be regarded as either a caricature of vulcanized rubber, or as a model of a chemical gel, or other soft random solid. It is a model very much in the spirit of lattice percolation, except that it naturally allows for particle motion as well as particle connectivity, and is therefore suitable for the study of continuum elasticity and other issues associated with the (thermal or deformational) motion of the constitute entities.

Equation (3.1) is a Hamiltonian for a given realization of quenched disorder \( \chi \equiv \{i_e, j_e\}_{e=1}^M \), which describes the particular random instance of the linking of the particles. These links are the quenched disorder of the system, which are specified at synthesis and do not change with thermal fluctuations, because there is a wide separation between the timescale for the linked-particle system to reach thermal equilibrium and the much longer timescale required for the links themselves to break. Therefore, in these systems we treat the links as permanent. Later, we shall apply the replica technique [39], which can appropriately deal with both the quenched and the annealed variables.

For a given volume and a given realization of disorder \( \chi \) we can write the partition function for the RLPM, \( Z_\chi \), as

\[
Z_\chi(V) \equiv \int_V \prod_{i=1}^N dc_i \exp \left( - \frac{H_\chi}{k_BT} \right) = Z_L(V) \left( \prod_{e=1}^M \Delta^{(0)}(c_{i_e} - c_{j_e}) \right)^{H_0},
\]  

(3.4)

where \( H_0 = \frac{a^2}{2} \sum_{i,j=1}^N \delta(c_i - c_j) \) is the excluded volume interaction part of the
Hamiltonian, and $Z_L(V) \equiv \int dV \prod_{i=1}^N dc_i \exp \left( -H_0/k_B T \right)$ is the partition function of the liquid in the absence of any links. The issue of the Gibbs factorial factor that is introduced to compensate for the overcounting of identical configurations is a genuinely subtle one in the context of random solids (for a discussion, see Ref. [8]). However, our focus will be on “observables” such as order parameter, rather than on free energies, and thus the omission of the Gibbs factor is of no consequence. The factor

$$\Delta^{(0)}(\vert c_{i_e} - c_{j_e} \vert) \equiv e^{-\frac{\vert c_{i_e} - c_{j_e} \vert^2}{2a^2}}$$

(3.5)

is associated with the link-induced attractive interaction term in the Hamiltonian. The average, $\langle \ldots \rangle^{H_0}_1$ taken with respect to a Boltzmann weight involving the excluded volume interaction Hamiltonian $H_0$, is defined as

$$\langle \ldots \rangle^{H_0}_1 \equiv \frac{1}{Z_L(V)} \int dV \prod_{i=1}^N dc_i e^{-\frac{H_0}{k_B T}} \ldots .$$

(3.6)

The corresponding Helmholtz free energy is then given by

$$F_{\chi}(V) \equiv -k_B T \ln Z_{\chi}(V).$$

(3.7)

To perform the average of the free energy over the quenched disorder, we shall need to choose a probability distribution that assigns a sensible statistical weight $P(\{i_e, j_e\}_{e=1}^M)$ to each possible realization of the total number $M$ and location $\{i_e, j_e\}_{e=1}^M$ of the links. Following an elegant strategy due to Deam and Edwards [16], we assume a version of the normalized links distribution as follows:

$$P(\chi) = \left( \frac{\eta^2 V_0}{2N\Delta_0^{(0)}} \right)^M Z_{\chi}(V_0) / M! Z_1,$$

(3.8)

where $V_0$ is the volume of the system at the instant the links are made, and $\eta^2$ is a parameter that controls the mean total number of links. The $Z_{\chi}(V_0)$ factor is actually the partition function, as given in Eq. (3.4), and can be regarded as probing the equilibrium correlations of the underlying unlinked liquid. The factor $\Delta_0^{(0)} = (2\pi a^2)^{d/2}$ is actually the $p = 0$ value of the Fourier transform of the $\Delta^{(0)}$ function defined in Eq. (3.5), and we shall see later that these factors ensures that the (mean-field) critical point occurs at $\eta^2 = 1$. The normalization factor $Z_1 \equiv \sum_{\chi} \left( \frac{\eta^2 V_0}{2N\Delta_0^{(0)}} \right)^M Z_{\chi}(V_0) / M!$. The calculation for $Z_1$ is straightforward, and is given in Appendix B.

The Deam-Edwards distribution can be envisaged as arising from a realistic vulcanization process in which the links are introduced simultaneously and instantaneously into the liquid state in equilibrium. Specifically, it incorporates the notion that all pairs of particles that happen (at some particular instant)
to be nearby are, with a certain probability controlled by the link density parameter $\eta^2$, linked. Thus, the correlations of the link-distribution reflect the correlations of the unlinked liquid, and it follows that realizations of links only acquire an appreciable statistical weight if they are compatible with some reasonably probable configuration of the unlinked liquid.

The factor $\left(\frac{\eta^2 V_0}{2N \Delta_{\eta}}\right)^M/M!$ of the Deam-Edwards distribution introduces a Poissonian character to the total number $M$ of the links, which are modeled to be the product of a Poissonian chemical process of linking. The factor $Z_\chi(V_0)$ assures that the probability of having a given random realization of links is proportional to the statistical weight for, in the unlinked liquid state, finding pairs that are to be linked being essentially co-located with one another, to within the shape $\exp\left(-|c_{i\epsilon} - c_{j\epsilon}|^2/2a^2\right)$.

As a result, the mean number of links per particle is given by $\frac{M}{N} = \frac{\eta^2}{2}$. Thus, $\eta^2 = 2[M]/N$ is the average coordination number, i.e., the average number of particles to which a certain particle is connected. For a detailed discussion of the Deam-Edwards distribution, see Ref. [16].

With this distribution of the quenched disorder, we can perform the disorder average of the Helmholtz free energy via the replica technique, thus obtaining

$$[F] = -k_B T \sum_\chi \mathcal{P}(\chi) F_\chi(V)$$

$$= -k_B T \sum_\chi \mathcal{P}(\chi) \ln Z_\chi(V)$$

$$= -k_B T \lim_{n \to 0} \sum_\chi \mathcal{P}(\chi) \frac{Z_\chi(V)^n - 1}{n}. \quad (3.9)$$

We now insert the Deam-Edwards distribution to get

$$[F] = -k_B T \lim_{n \to 0} \sum_\chi \left(\frac{\eta^2 V_0}{2N \Delta_{\eta}}\right)^M \frac{Z_\chi(V_0)}{M!Z_1} \frac{Z_\chi(V)^n - 1}{n}. \quad (3.10)$$

This disorder-averaged free energy differs from the form traditionally obtained via the replica technique, in that there is an extra replica $Z_\chi(V_0)$, which originates in the Deam-Edwards distribution. We shall call this extra replica the 0-th replica, and note that it represent the preparation state of the system.

The summation over the realizations of the quenched disorder $\chi$ can be performed, following the calculation in Appendix B; thus we arrive at the form

$$[F] = -k_B T \lim_{n \to 0} \frac{1}{n} \left(\frac{Z_{1+n}}{Z_1} - 1\right), \quad (3.11)$$

which can also be expressed as

$$[F] = -k_B T \lim_{n \to 0} \frac{\partial}{\partial n} \ln Z_{1+n} \quad (3.12)$$
where

\[
Z_{1+n} = \sum_{\chi} \left( \frac{\eta^2 V_0}{2N\Delta(0)} \right)^{M} Z_{\chi}(V_0) Z_{\chi}(V)^n = Z_{\mathcal{E}}(V_0) Z_{\mathcal{E}}(V)^n \left\{ \exp \left( \frac{\eta^2 V_0}{2N\Delta(0)} \sum_{i \neq j}^{N} \prod_{\alpha=0}^{n} \Delta^{(0)} \left( |c_{i\alpha}^\beta - c_{j\alpha}^\beta| \right) \right) \right\}^{H_0}_{1+n}. \tag{3.13}
\]

Notice that here the preparation state (replica 0) has a fixed volume \(V_0\) because, for convenience, we have assumed that the linking process was undertaken instantaneously in a liquid state of fixed volume, whereas the measurement states (replicas 1 through \(n\)) are put in a fixed pressure \(p\) environment, the volume \(V\) of which is allowed to fluctuate. In the latter parts of this Thesis, we shall set the pressure \(p\) to be the average pressure measured at the preparation state at \(V_0\). In particular, for a given volume of the liquid state in which the links are made, the average pressure is given by

\[
p = -\frac{\partial F_{\mathcal{L}}(V_0)}{\partial V_0} \bigg|_T, \tag{3.14}
\]

where we have introduced the Helmholtz free energy of the unlinked liquid \(F_{\mathcal{L}}(V_0) \equiv -k_B T \ln Z_{\mathcal{L}}(V_0)\). Supposing that the excluded volume interactions are so strong that the density of the unlinked liquid is just \(N/V_0\) and all fluctuations of the density are suppressed, we have for the mean-field value of Helmholtz free energy in the unlinked liquid state:

\[
F_{\mathcal{L}}(V_0) = -NK_B T \ln V_0 + \frac{\nu^2 N^2}{2V_0}. \tag{3.15}
\]

Therefore, the mean pressure in the unlinked liquid state is given by

\[
p = \frac{NK_B T}{V_0} + \frac{\nu^2 N^2}{2V_0^2}. \tag{3.16}
\]

As mentioned above, we shall keep this pressure in the measurement states (replicas), and let the volume \(V\) fluctuate, in order to obtain an elastic free energy that can describe volume variation, in particular, by choosing the pressure \(p\) to be exactly the mean pressure in the liquid state, we shall obtain an elastic free energy that takes the state right after linking, which has the same volume \(V_0\) as the liquid state, as the elastic reference state. This issue about state right after linking and the elastic reference state will be discussed in detail in Section 4.1.

Through this construction, we are in a position to learn about the bulk modulus of the system, and to characterize the volume change caused by linking, which has the effect of eliminating translational degrees of freedoms.

To establish an appropriate statistical mechanics for the fixed-pressure ensemble, we shall make the following Legendre transformation of the Helmholtz
free energy, which leads to the Gibbs free energy $G(p,T)$:

$$p = -\frac{\partial F(V,T)}{\partial V} \bigg|_T,$$  \hspace{1cm} (3.17a)

$$G(p,T) = F(V,T) + pV,$$ \hspace{1cm} (3.17b)

where in Eq. (3.17b) the volume $V$ takes the value (in terms of $p$) that satisfies Eq. (3.17a), which is the volume that minimizes the Gibbs free energy with a given pressure $p$.

In the following sections, we shall first calculate the disorder average of the Helmholtz free energy, and then make this Legendre transformation to obtain the disorder-averaged Gibbs free energy, and this will allows us to develop a detailed exploration of the elasticity of the RLPM.

### 3.2 Field-theoretic description

We shall use field-theoretic methods to analyze the disorder-averaged free energy $\mathbb{F}$ and, more specifically, the replicated partition function $Z_{1+n}$. To do this, we introduce the replicated density function

$$Q(\hat{x}) \equiv \frac{1}{N} \sum_{j=0}^{N} \prod_{\alpha=0}^{n} \delta^{(d)}(x^\alpha - c^\alpha_j),$$ \hspace{1cm} (3.18)

where $\hat{x} \equiv (x^0, x^1, \ldots, x^n)$ is a shorthand for the $(1+n)$-fold replicated position $d$-vector. For convenience, we introduce a complete orthonormal basis set in replica space $\{\epsilon^\alpha\}_{\alpha=0}^{n}$, in terms of which a vector $\hat{x}$ can be expressed as

$$\hat{x} = \sum_{\alpha=0}^{n} x^\alpha \epsilon^\alpha.$$ \hspace{1cm} (3.19)

Note that the components are themselves $d$-vectors.

The replicated partition function can be written as a functional of the replicated density function $Q$ as

$$Z_{1+n} = \int_{V_0} \prod_{i=1}^{N} dc_i^0 \int_{V} \prod_{\alpha=0}^{n} \prod_{j=1}^{N} dc_j^\alpha \ e^{-\frac{H_Q[Q]}{k_BT}},$$ \hspace{1cm} (3.20)

with

$$H_Q[Q] \equiv -\frac{N \eta^2 k_BT}{2V^n \Delta_0^{(0)}} \sum_{p} Q_p Q_{-p} \Delta^{(1+n)}_p + \frac{\nu^2 N^2}{2V_0} \sum_{p} Q_{pe^0} Q_{-pe^0} + \frac{\nu^2 N^2}{2V} \sum_{p} \sum_{\alpha=1}^{n} Q_{pe^\alpha} Q_{-pe^\alpha},$$ \hspace{1cm} (3.21)

where $Q_{\hat{p}}$ is the Fourier transform of $Q(\hat{x})$, which is defined in Eq. (3.18), and
the factor
\[ \Delta_p^{(1+n)} = \left( \Delta_0^{(0)} \right)^{1+n} e^{-\alpha^2 \Delta_p^2/2} \quad (3.22) \]
is the replicated version of the Fourier transform of the function \( \Delta^{(0)}(x) \), which is defined in Eq. (3.5).

The first term on the right hand side of Eq. (3.21) arises from the attractive, link-originating, interaction part [see Eq. (3.13)]; the next two terms represent the excluded volume interaction in \( H_0 \), for the 0-th replica and for replicas 1 through \( n \), respectively.

Because the excluded volume interaction is very strong, and thus the density fluctuations in any single replica are heavily suppressed. This has been discussed in the construction of the Landau theory, in Section 1.3.4, where one can separate the order parameter into HRS and LRS. With this separation, we can rewrite the effective Hamiltonian as
\[ H_Q[\hat{Q}_p] = -\frac{N\eta^2 k_B T}{2Vn\Delta_0^{(0)}} \sum_{\hat{p} \in \text{HRS}} Q_pQ_{-\hat{p}}\Delta_p^{(1+n)} + \frac{\tilde{\nu}_0^2(p)N^2}{2V_0} \sum_p Q_{p\omega^*}Q_{-p\omega^*} \]
\[ + \frac{\tilde{\nu}_0^2(p)N^2}{2V} \sum_p \sum_{\alpha=1}^n Q_{p\omega^*}Q_{-p\omega^*}, \quad (3.23) \]
where we kept the LRS for the moment, and with the renormalized coefficients
\[ \tilde{\nu}_0^2(p)N^2 \equiv \frac{\nu^2 N^2}{2V} - \frac{N\eta^2 k_B T \Delta_p^{(1+n)}}{2Vn\Delta_0^{(0)}}, \]
\[ \tilde{\nu}_0^2(p)N^2 \equiv \frac{\nu^2 N^2}{2V} - \frac{N\eta^2 k_B T \Delta_p^{(1+n)}}{2Vn\Delta_0^{(0)}}. \quad (3.24) \]
We suppose that \( \frac{\nu^2 N^2}{2V} \gg \eta^2 \) (i.e., the excluded volume repulsion is very strong, relative to the attractive effects of the links), so these coefficients \( \tilde{\nu}_0^2(p)N^2 \) are always positive and large, relative to the energyscale of the HRS that we are interested.

The Hamiltonian (3.24) can be analyzed using a Hubbard-Stratonovich (HS) transformation (for details see Appendix C). Via this HS transformation, the interactions between particles can be decoupled. Thus, we arrive at a field-theoretic formulation of the replicated partition function:
\[ Z_{1+n} = \int D\Omega_p \prod_{\alpha=0}^n D\Omega_{p\alpha} e^{-\frac{H_{Q[\Omega_{\alpha}]}}{k_B T}}, \quad (3.25) \]
where the effective Hamiltonian is given by

\[ H_{\Omega}[\Omega^\alpha, \hat{\Omega}^\rho] = \frac{N\eta^2 k_B T}{2V^n \Delta_0^{(0)}} \sum_{\rho \in \text{HRS}} \Omega^\rho \Omega - \hat{\rho}^\rho \Delta_p^{(1+n)} + \frac{\tilde{\rho}^2 N^2}{2V_0} \sum_p \Omega_{pe^0} \Omega_{pe^0} \\
+ \frac{\tilde{\rho}^2 N^2}{2V} \sum_p \sum_{\alpha=1}^n \Omega_{pe^0} \Omega_{pe^0} - Nk_B T \ln z_0. \tag{3.26} \]

and

\[ z_0 = \int_{V_0} \int_{V_0} \prod_{k=0}^n \int_{V_0} \int_{V_0} \exp \left[ \frac{-\eta^2}{V^n \Delta_0^{(0)}} \sum_{\rho \in \text{HRS}} \Omega^\rho \Delta_p^{(1+n)} e^{i\hat{\rho}^\rho} \right] \\
+ \frac{i\tilde{\rho}^2 N}{V_0 k_B T} \sum_p \Omega_{pe^0} e^{i\hat{\rho}^\rho} + \frac{i\tilde{\rho}^2 N}{V k_B T} \sum_p \sum_{\alpha=1}^n \Omega_{pe^0} e^{i\hat{\rho}^\rho}. \tag{3.27} \]

The form of this HS transformation [see Appendix C, especially Eq. (C.5)] enforce that the averages of the \( Q \) field and the \( \Omega \) field obey the relations

\[ \langle Q^\rho \rangle_{H_Q} = \langle \Omega^\rho \rangle_{H_\Omega}, \tag{3.28a} \]
\[ i\langle Q^\rho \rangle_{H_Q} = \langle \Omega^\rho \rangle_{H_\Omega}, \tag{3.28b} \]

where the two averages are defined as

\[ \langle \cdots \rangle_{H_Q} = \frac{1}{Z_{1+n}} \int V_0 \prod_{i=1}^N \int V_0 \prod_{\alpha=0}^n \int V_0 \pi \sum_{\bar{\pi}} e^{-\frac{\eta^2}{V^n \Delta_0^{(0)}} \sum_{\rho \in \text{HRS}} \Omega^\rho \Delta_p^{(1+n)} \pi_{Q^\rho}^{\Omega^\rho} \cdots}, \tag{3.29a} \]
\[ \langle \cdots \rangle_{H_\Omega} = \frac{1}{Z_{1+n}} \int D\Omega \prod_{\alpha=0}^n D\Omega e^{-\frac{\eta^2}{V^n \Delta_0^{(0)}} \sum_{\rho \in \text{HRS}} \Omega^\rho \Delta_p^{(1+n)} \sum_{\alpha=0}^n \pi_{Q^\rho}^{\Omega^\rho} \cdots}. \tag{3.29b} \]

There are also related equalities for higher-order statistical moments, as discussed in Appendix C.

The leading-order terms in \( H_{\Omega}[\Omega^\alpha, \hat{\Omega}^\rho] \) can be constructed by expanding the \( \ln z_0 \) term in Eq. (3.26) in powers of the fields \( \Omega^\rho \) and \( \Omega_{pe^0} \), and thus we can obtain the leading-order terms in the Landau-Wilson effective Hamiltonian. The leading order expansion is

\[ H_{\Omega}[\Omega_{pe^0}, \hat{\Omega}^\rho] = \frac{N\eta^2 k_B T}{2V^n \Delta_0^{(0)}} \sum_{\rho \in \text{HRS}} \Omega^\rho \Omega - \hat{\rho}^\rho \Delta_p^{(1+n)} \left( 1 - \frac{\eta^2}{V^n \Delta_0^{(0)}} \right) \\
+ \frac{\tilde{\rho}^2 N^2}{2V_0} \sum_p \Omega_{pe^0} \Omega_{pe^0} \left( 1 + \frac{\tilde{\rho}^2 N}{V_0 k_B T} \right) \\
+ \frac{\tilde{\rho}^2 N^2}{2V} \sum_p \sum_{\alpha=1}^n \Omega_{pe^0} \Omega_{pe^0} \left( 1 + \frac{\tilde{\rho}^2 N}{V k_B T} \right) + O((\Omega_{pe^0})^3, (\Omega^\rho)^3). \tag{3.30} \]

For the LRS fields, \( \Omega_{pe^0} \), we see the coefficients of the corresponding quadratic
term are always positive (given \( \tilde{\nu}^2, \tilde{\rho}^2 > 0 \), i.e., the excluded volume repulsion is very strong), so this sector of the field theory does not undergo an instability. Furthermore, because these coefficients (the masses, in particle-physics language) are very large [see Eq. (3.24)], the fluctuations of these LRS fields \( \Omega_{p\epsilon^\alpha} \) are heavily suppressed. For this reason, we ignore these fluctuations and, for all \( \alpha = 0, 1, \ldots, n \), we take

\[
\Omega_{p\epsilon^\alpha}|_{p=0} = 1 \\
\Omega_{p\epsilon^\alpha}|_{p \neq 0} = 0
\]  

(3.31)

as a hard constraint. This justifies the same constraint we took in constructing the Landau free energy of random solidification transition transitions in Section 1.3.4, from the microscopic perspective.

Having implemented this constraint, we arrive at the HRS Hamiltonian (the full form, not the just leading-order expansion):

\[
H_\Omega[\hat{\Omega}] = \frac{N\eta^2 k_B T}{2 V n \Delta_0} \sum_{\hat{\rho} \in \text{HRS}} \Omega_{\hat{\rho}} \Omega_{-\hat{\rho}} \Delta_{\hat{\rho}}^{(1+n)} - Nk_B T \ln z_0,
\]

where

\[
z_0 = \int_{V_0} dc^0 \int_{V} \prod_{\alpha=0}^{n} dc^\alpha \exp \left[ \frac{\eta^2}{V n \Delta_0} \sum_{\hat{\rho} \in \text{HRS}} \Omega_{\hat{\rho}} \Delta_{\hat{\rho}}^{(1+n)} e^{i \hat{\rho} \cdot \hat{c}} \right].
\]

(3.33)

The Landau theory of the vulcanization transition [44] can be recovered by making an expansion of this HRS Hamiltonian that keeps only the leading-order terms in the order parameter \( \Omega \) and the momentum \( \hat{\rho} \). Up to an additive constant and an appropriate rescaling of the order parameter, this expansion reads

\[
H_\Omega[\hat{\Omega}] = \frac{1}{2} \sum_{\hat{\rho} \in \text{HRS}} (r + |\hat{\rho}|^2) \Omega_{\hat{\rho}} \Omega_{-\hat{\rho}} - \frac{v}{3!} \sum_{\hat{\rho}_1, \hat{\rho}_2 \in \text{HRS}} \Omega_{\hat{\rho}_1} \Omega_{\hat{\rho}_2} \Omega_{-\hat{\rho}_1 - \hat{\rho}_2},
\]

(3.34)

where the potential of the links \( \Delta_{\hat{\rho}}^{(1+n)} \) is momentum-expanded. This is precisely the form of the Landau free energy we discussed in Section 1.3.4, which is constructed by symmetry argument. In the limit \( n \to 0 \), the coefficients becomes

\[
r \propto \eta^2 (1 - \eta^2), \\
v \propto (\eta^2)^3.
\]

(3.35)

It is straightforward to see that the \( r \) term leads to an instability for \( \eta^2 > 1 \) (in the limit of \( n \to 0 \)), corresponding to a link density larger than some critical value, and the lowest unstable modes are long-wavelength modes (i.e., \( \hat{\rho} \to 0 \)). [One should, however, keep in mind that the component \( \hat{\rho} = 0 \) itself, which is the 0RS, is excluded from this HRS-only field theory; see Eq. (3.31).] This
instability corresponds to the liquid-to-soft random solid transition, because the liquid state corresponds to the $\Omega_{\hat{p}} = 0$ (in HRS) state and becomes unstable when the link density parameter $\eta^2$ exceeds 1.

As discussed in Section 3.1, we have assumed that the potential due to the soft links is a Gaussian chain potential [see Eq. (3.2,3.5)]. Here, it is evident that the phase transition from the liquid state to the random solid state is governed by only the long-distance or small-momentum behavior of the theory, and we only kept terms to $|\hat{p}|^2$ in $\Delta_{\hat{p}}^{(1+n)}$. Therefore, even if we were to change to a different potential [e.g., the covalent bond as in Eq. (3.3)], the fact that its leading-order (in momentum-space) is of the same form, ensures that the transition would not be affected by this microscopic detail. Furthermore, as we shall see in subsequent sections, the entropic elasticity of this model network is a result of thermal fluctuations, and does not depend on any particular choice of the microscopic interaction.

### 3.3 Mean-field theory

To see the form of the stationary value of the order parameter in vulcanization theory, we shall first take a look at its physical meaning.

The properties of the HS transformation, Eq. (3.28a), relate the stationary-point order parameter $\Omega$ to the thermal average of the replicated density function $Q$. According to this relation, we have

$$\Omega_{\hat{p}} \to \frac{1}{N} \sum_{j=1}^{N} e^{i\hat{p} \cdot \hat{c}_j} - \delta_{\hat{p}}^{(1+n)d}.$$  \hfill (3.36)

Here, the $\delta_{\hat{p}}^{(1+n)d}$ removes the 0RS part. Equivalently, in real space we have

$$\Omega(\hat{x}) \to \frac{1}{N} \sum_{j=1}^{N} \delta^{(1+n)d}(\hat{x} - \hat{c}_j) - \frac{1}{V_0 V^n}.$$  \hfill (3.37)

The statistical average of this field, weighted with the Hamiltonian $H_{\Omega}$, Eq. 3.32, is

$$\langle \Omega(\hat{x}) \rangle_{H_{\Omega}} = \langle \frac{1}{N} \sum_{j=1}^{N} \delta^{(1+n)d}(\hat{x} - \hat{c}_j) \rangle_{H_Q} - \frac{1}{V_0 V^n}$$

$$= \left[ \langle \delta^{(d)}(x^0 - c^0_j) \rangle \langle \delta^{(d)}(x^1 - c^1_j) \rangle \cdots \langle \delta^{(d)}(x^n - c^n_j) \rangle \right] - \frac{1}{V_0 V^n},$$  \hfill (3.38)

where, on the second line, we have interpreted the average of the replicated system with the Hamiltonian $H_Q$ as follows: One first constructs independent thermal averages in each replica (denoted by $\langle \cdots \rangle$) with a common given realization of disorder $\chi$; one then forms the product over all replicas, and finally one averages over all realizations of disorder (an average denoted by $[\cdots]$).
This interpretation can be understood from the definition of \( H_Q \) via \( Z_{1+n} \) as in Eq. (3.20). Recall that \( Z_{1+n} \), as defined in Eq. (3.13), contains \((1 + n)\) thermal averages of the \((1 + n)\) replicas, represented by the factor \( Z_{\chi}(V_0)Z_{\chi}(V)^n \), with an overall disorder average. This validates the interpretation given in Eq. (3.38) [and also in Eq. (1.22)]. For a strict proof, see Ref. [8].

The meaning of this order parameter, and the reason why it can distinguish the liquid state and the random solid state, has been discussed in Sections 1.3.3 and 1.3.4, which lead to the following hypothesized form for the stationary value of the order parameter in real space:

\[
\Omega(\hat{x}) = Q \int \frac{dz}{V_0} \int d\tau P(\tau) \left( \frac{\tau}{2\pi} \right)^{\frac{1+n}{2}} e^{-\frac{\tau}{2}(|x_0 - z|^2 + \sum_{\alpha=1}^n |x_\alpha - \zeta z|^2)} - \frac{Q}{V_0 V^n},
\]

which is parameterized by \( Q \) (i.e., the fraction of particles that are localized) and \( P(\tau) \) (i.e., the distribution of inverse square localization lengths), where \( \tau \equiv 1/\xi^2 \) is the inverse square localization lengths, \( \xi \) is the localization length. In addition, the contraction \( \zeta \) is related to the change of volume as

\[
\frac{V}{V_0} = \zeta^d.
\]

We can also write this stationarity point order parameter in momentum space:

\[
\Omega_{\hat{p}} = Q \int \frac{dz}{V_0} \int d\tau P(\tau) e^{-\frac{|\hat{p}|^2}{4\tau} - i\hat{p} \cdot z - i\sum_{\alpha=1}^n \hat{p} \cdot (\zeta z)} - Q\delta_{\hat{p}}^{(1+n)d}.
\]

The parameters that characterize this order parameter, \( Q \) and \( P(\tau) \), have been obtained by solving the stationarity condition for the Hamiltonian:

\[
\frac{\delta H_{\Omega}}{\delta \Omega_{\hat{p}}} = 0.
\]

In particular, the equation for \( Q \) is

\[
1 - Q = e^{-\eta^2 Q}.
\]

For all values of \( \eta^2 \), Eq. (3.43) has a solution \( Q = 0 \), corresponding to the liquid state. However, for \( \eta^2 > 1 \), an additional root appears, emerging continuously from \( Q = 0 \) at \( \eta^2 = 1 \), and describing the equilibrium amorphous solid state. In Fig. 5.1 we show the dependence of the localized fraction on the link density, which we characterize by \( \eta^2 \). For a detailed discussion and for the stationary-point distribution of inverse square localization lengths \( P(\tau) \), see Refs. [8, 43].

The contraction \( \zeta \), which is relevant to the elasticity of the random solid state, can be investigated by inserting this form of the order parameter, Eq. (3.41), into the Hamiltonian \( H_{\Omega} \), Eq. (3.32), and this yields the dependence of the
Hamiltonian on the parameters \( Q, P(\tau) \) and \( \zeta \). Through a tedious derivation, and by keeping terms to \( O(n) \), we have the following Hamiltonian for the stationary point (cf. Appendix D):

\[
H^{(SP)}_{12} = \frac{\tilde{\nu}^2(0)N^2}{2V_0} + \frac{n\tilde{\nu}^2(0)N^2}{2V} - Nk_B T \ln V_0 - nNk_B T \ln V
+ nNk_B T \left\{ \frac{d}{2} \left( \ln(2\pi) + \zeta^2 \right) - \ln V \right\}
- \frac{\eta^2 Q^2}{2} \cdot \frac{d}{2} \int_{\tau_1,\tau_2} \ln \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2 \right)
- e^{-\eta^2 Q^2} \frac{d}{2} \sum_{m=1}^{\infty} (\eta^2 Q)^m \frac{(\eta^2 Q)^m}{m!} \int_{\tau_1,\ldots,\tau_2} \ln \left( \frac{\tilde{\tau}_1 \cdots \tilde{\tau}_m}{\tau_1 + \cdots + \tilde{\tau}_m} \right). \tag{3.44}
\]

Here, the variable \( \tilde{\tau} \) is defined as \( \tilde{\tau} \equiv \left( \frac{1}{\tau_1} + a^2 \right)^{-1} \). The dimensionless factor \( \theta \) in Eq. (3.44) is given by

\[
\theta \equiv -\frac{\eta^2 Q^2}{2} + \eta^2 Q - 1 + e^{-\eta^2 Q}. \tag{3.45}
\]

We shall see in Chapter 5 that the parameter \( \theta \) also gives the mean shear modulus, as well as the amplitude of the correlations involving the residual stress fields.

To obtain the disorder-averaged free energy, we shall make the saddle point approximation:

\[
Z_{1+n} \simeq e^{-F_{SP}^{(SP)}}. \tag{3.46}
\]

Thus, we can get the Helmholtz free energy using Eq. (3.11), and arrive at

\[
[F_{SP}] = -k_B T \lim_{n \to 0} \frac{1}{n} \left( \frac{Z_{1+n}}{Z_1} - 1 \right)
= -Nk_B T \left( 1 - \frac{\eta^2}{2} + \theta \right) \ln V - Nk_B T \frac{\theta d}{2} \left( \ln(2\pi) + \zeta \right) + \frac{\eta^2 N^2}{2V}
- \frac{\eta^2 Nk_B}{2} \ln \Delta_0^{(0)} + Nk_B T \frac{\eta^2 Q^2}{2} \frac{d}{2} \int_{\tau_1,\tau_2} \ln \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2 \right)
+ Nk_B T \frac{d}{2} e^{-\eta^2 Q^2} \sum_{m=1}^{\infty} (\eta^2 Q)^m \frac{(\eta^2 Q)^m}{m!} \int_{\tau_1,\ldots,\tau_2} \ln \left( \frac{\tilde{\tau}_1 \cdots \tilde{\tau}_m}{\tau_1 + \cdots + \tilde{\tau}_m} \right), \tag{3.47}
\]

where we have used the mean-field value of \( Z_1 \) in Eq. (B.3), and we have also made an expansion for small \( n \) of the renormalized excluded volume parameter \( \tilde{\nu}^2 \), using

\[
\Delta_0^{(1+n)} = (\Delta_0^{(0)})^{1+n}
= \Delta_0^{(0)} (1 + n \ln \Delta_0^{(0)} + O(n^2)). \tag{3.48}
\]
In order to study elasticity, we shall need to know the disorder-averaged Gibbs free energy $[G]$, which is given by a Legendre transformation, Eq. (3.17):

$$[G_{SP}] = [F_{SP}] + pV.$$  \hspace{1cm} (3.49)

We can insert the pressure $p$, given by Eq. (3.16) and, in the limit $\nu^2 N k_B T V \gg \eta^2 \gg 1$ (in which the coefficient of $\ln V$ becomes $\theta \simeq \eta^2 / 2 - 1$), we arrive at

$$[G_{SP}] \simeq \nu^2 N^2 2 V_0 \left[ 2 + \left( \frac{V}{V_0} - 1 \right)^2 \right] - N k_B T \frac{\theta d}{2} \left( \ln(2\pi) + \zeta^2 \right)$$

$$- \frac{\eta^2}{2} \ln \Delta_0^{(0)} + \frac{N k_B T \eta^2 Q^2}{2} \int_{\tau_1, \tau_2} \ln \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2 \right)$$

$$+ N k_B T \frac{d}{2} e^{-\eta^2 Q} \sum_{m=1}^{\infty} \frac{(\eta^2 Q)^m}{m!} \int_{\tau_1, \ldots, \tau_2} \ln \left( \frac{\tilde{\tau}_1 \cdots \tilde{\tau}_m}{\tau_1 + \cdots + \tau_m} \right).$$  \hspace{1cm} (3.50)

By using the relation (3.40), we can obtain the stationary contraction $\zeta$ that minimize the disorder-averaged Gibbs free energy by solving

$$\frac{\delta[G_{SP}]}{\delta \zeta} = 0.$$  \hspace{1cm} (3.51)

In the limit $\frac{\nu^2 N}{k_B T V} \gg \eta^2 \gg 1$, the solution is

$$\zeta \simeq 1 - \frac{\theta V_0 k_B T}{\eta^2 N d}.$$  \hspace{1cm} (3.52)

The limit $\frac{\nu^2 N}{k_B T V} \gg \eta^2$ is the same as the limit taken below Eq. (3.24), indicating that the excluded volume repulsion is much stronger than the attractive effects of the links. The limit $\eta^2 \gg 1$ indicates that we are concerned with the well-linked regime (rather than the transition regime). This contraction of the volume due to introduction of links at a given pressure is a result of the reduction of the total number of degrees of freedom, \textit{i.e.}, the change of the “osmotic pressure”. We shall see later that this reduction is consistent with a particular phenomenological model of a disordered elastic medium that we shall introduce.

### 3.4 Goldstone fluctuations

#### 3.4.1 Spontaneous symmetry breaking

To characterize the Goldstone family of fluctuations associated with the random solid state, we shall first look at the pattern of symmetry breaking accompanying with the transition to this state. The Hamiltonian (3.32) for the liquid to soft-random-solid transition has the symmetry of independent translations and rotations of each replica. The translational invariance of the Hamiltonian can be easily verified by making the
transformation

\[ \hat{x} \rightarrow \hat{x}' = \hat{x} + \hat{a}, \]
\[ \Omega(\hat{x}) \rightarrow \Omega'(\hat{x}') = \Omega(\hat{x} - \hat{a}), \quad (3.53) \]

where \( \hat{a} \equiv (a^0, a^1, \ldots, a^n) \) represents a replicated translation. In momentum space, this transformation reads

\[ \Omega_{\hat{p}} \rightarrow \Omega'_{\hat{p}} = e^{i\hat{p} \cdot \hat{a}} \Omega_{\hat{p}}. \quad (3.54) \]

It is easy to find that by inserting this transformed order parameter back into the Hamiltonian (3.32) and making a change of variables, the same Hamiltonian but for the field \( \Omega' \) is recovered. Similarly, one can verify invariance under independent rotations \( \hat{O} \equiv (O^0, O^1, \ldots, O^n) \) with

\[ \Omega_{\hat{p}} \rightarrow \Omega'_{\hat{p}^{-1}/\hat{O}}. \quad (3.55) \]

The order parameter in the liquid state (i.e., \( \Omega = 0 \)) has the full symmetry, and at the transition to the soft random solid state, it is the symmetry of relative translations and rotations between different replicas that is spontaneously broken. However, the symmetry of common translations and rotations of all replicas are preserved, and this reflects the important notion that, from the macroscopic perspective the system remains translationally and rotationally invariant, even in the random solid state. This entire pattern amounts to an unfamiliar but essentially conventional example of the Landau paradigm.

This broken symmetry of relative translations and rotations between different replicas can be understood as a result of particle localization. Because a delocalized liquid particle can explore the whole volume via its thermal fluctuations, and in thermal equilibrium its positions in each replica are uncorrelated, the liquid state is invariant, if one translates (or rotates) the replicas in different directions. On the contrary, for a localized particle, its positions in the various replica are strongly correlated, and therefore the symmetries of relative translations and rotations are broken.

It is easy to verify that the form of the random-solid-state order parameter, Eq. (3.39), correctly implements this pattern of symmetry breaking. To see this, we can use the complete orthonormal basis in replica space defined in Section 3.2, and define an alternative basis involving a “replica body-diagonal” unit vector

\[ \hat{\epsilon}_\lambda \equiv \frac{1}{\sqrt{1 + n\zeta^2}} \left( \epsilon^0 + \zeta \sum_{\alpha=1}^{n} \epsilon^\alpha \right). \quad (3.56) \]

Relative to \( \hat{\epsilon}_\lambda \), we may decompose a \((1 + n)d\) dimensional vector \( \hat{x} \) into its
longitudinal ($\lambda$) and transverse ($\tau$) components:

$$\hat{x} = \hat{x}_\lambda + \hat{x}_\tau, \quad \hat{x}_\lambda = (\hat{x} \cdot \hat{\epsilon}_\lambda)\hat{\epsilon}_\lambda, \quad \hat{x}_\tau = \hat{x} - \hat{x}_\lambda.$$  \hfill (3.57)

Note that $\hat{x}_\lambda$ and $\hat{x}_\tau$ are both $(1 + n)d$ dimensional vectors, but $\hat{x}_\lambda$ has only $d$ degrees of freedom (given by $\hat{x} \cdot \hat{\epsilon}_\lambda$), and $\hat{x}_\tau$ has $nd$ only degrees of freedom.

By this decomposition, the vector $\hat{z} = (z, \zeta z_1, \zeta z_2, \ldots)$, which characterizes the mean positions in the stationary state, can be written as

$$\hat{z} = \sqrt{1 + n\zeta^2} \hat{\epsilon}_\lambda,$$  \hfill (3.58)

which is purely in the $\hat{\epsilon}_\lambda$ direction. As a result, the stationary order parameter, Eq. (3.39), can be written as

$$\Omega_{SP}(\hat{x}) = Q \int \frac{dz}{V_0} \int d\tau P(\tau) \left( \frac{\tau}{2\pi} \right)^{(1+n)d/2} e^{-\frac{z}{2} |\hat{x}_\lambda - \hat{x}_\lambda(z)|^2 - \frac{1}{\tau(1+n\zeta^2)}} - \frac{Q}{V_0 V^n},$$  \hfill (3.59)

where in the last line we have integrated out the $d$-dimensional vector $z$. It is evident that this value of order parameter does not depend on $\hat{x}_\lambda$, which means that it is invariant under translations in the $\hat{\epsilon}_\lambda$ direction, corresponding to common translations and rotations of all replicas (albeit appropriately contracted by $\zeta$ in replicas 1 through $n$). This stationary order parameter is schematically drawn in Fig. 3.4.2 for two replicas. The Gaussian form in the $\hat{x}_\tau$ direction indicates a “condensation” between different replicas. This is called a molecular bound state in Ref. [56].

### 3.4.2 Goldstone modes

With the pattern of continuous symmetry breaking just outlined, we can write down the form that the order parameter takes when it is subject to Goldstone fluctuations:

$$\Omega_{GS}(\hat{x}) = Q \int \frac{dz}{V_0} \int d\tau P(\tau) \left( \frac{\tau}{2\pi} \right)^{(1+n)d/2} e^{-\frac{z}{2} |\hat{x}_\lambda - R^i(z)|^2} - \frac{Q}{V_0 V^n}.$$  \hfill (3.60)

The “Goldstone distortion” of the order parameter is parameterized by the $n$ functions $\{R^1(z), \ldots, R^n(z)\}$, with the function $R^0(z)$ being defined to be $z$ itself. The stationary form of the order parameter, Eq. (3.39), describes a system in which the mean positions of the replicas of the thermally fluctuating particle are located at positions $(x_0, x_1, \ldots, x_n) = (z, \zeta z, \ldots, \zeta z)$. We shall refer to these positions as the “center of the thermal cloud”. By comparing the undeformed order parameter (3.39) and the “Goldstone-deformed” one, Eq. (3.60), we see that the Goldstone-deformed order parameter describes a system in which the
mean positions of the replicas of the fluctuating particle are displaced from
\( (z, \zeta z, \ldots, \zeta z) \) to \( (z, R^\alpha(z), \ldots, R^\alpha(z)) \). Thus, \( R^\alpha(z) (\alpha = 1, 2, \ldots, n) \) represent the deformed mean positions of the measurement replicas.

We require that the deformations \( \zeta z \rightarrow R^\alpha(z) \) be pure shear deformations; this constraint can be expressed as \( \det(\partial R^\alpha_i(z)/\partial(\zeta z)_j) = 1 \). It guarantees that the Goldstone mode does not excite the LRS \( \text{i.e.,} \) does not change any single-replica density, which would be extremely energetically costly, owing to the large excluded volume interaction. The 0RS has already been removed from the theory, and one can easily check that it remains zero in this Goldstone-deformed order parameter. The vanishing of the order parameter in the 1RS can be verified by taking the momentum-space Goldstone mode and making a change of variables:

\[
\begin{align*}
(\Omega_{GS})_{\mu\nu} &= Q \int \frac{dz}{V_0} \int d\tau P(\tau) e^{-\frac{|p|^2}{2\tau} - ip R^\alpha(z)} - Q\delta^{(1+n)d}_p \\
&= Q \int \frac{dR^\alpha}{V} \left| \frac{\partial z}{\partial R^\alpha} \right| \int d\tau P(\tau) e^{-\frac{|p|^2}{2\tau} - ip R^\alpha(z)} - Q\delta^{(1+n)d}_p \\
&= 0. \tag{3.61}
\end{align*}
\]

This indicates that the deformed state has the same density as the stationary point state.

There are two points that we need to clarify about this Goldstone mode. First, as we have already mentioned, the symmetry broken at the transition is that of relative translations and rotations of the various replicas, the symmetry of common translations and rotations remaining intact. As a result, the Goldstone mode should be constructed via \( z \)-dependent translations of the order parameter in the \( \hat{x}_\tau \) direction, \text{i.e.,} the the broken symmetry direction. However, if we look at the deformation field defined by \( \hat{U} \equiv \hat{R} - \hat{z} \), we find that \( \hat{U} = \{0, R^1(z) - \zeta z, R^2(z) - \zeta z, \ldots\} \) is in fact not in the broken symmetry direction \( \hat{x}_\tau \), because it has a \( \hat{x}_\lambda \) component, namely,

\[
\hat{U}_\lambda = (\hat{U} \cdot \hat{e}_\lambda) \hat{e}_\lambda = \frac{\zeta}{\sqrt{1 + n\zeta^2}} \sum_{\alpha=1}^n U^\alpha(z) \hat{e}_\lambda \tag{3.62}
\]

This \( \hat{U}_\lambda \) component is actually redundant. This can be seen by decomposing the quadratic form \( |\hat{x} - \hat{z} - \hat{U}|^2 \) as:

\[
|\hat{x} - \hat{z} - \hat{U}|^2 = |\hat{x}_\lambda - \hat{z}_\lambda - \hat{U}_\lambda|^2 + |\hat{x}_\tau - \hat{U}_\tau|^2, \tag{3.63}
\]

and noting that in the form of the order parameter (3.60) one can change the integration variable (which is a \( d \)-dimensional vector) from \( z \) to

\[
y \equiv z + \frac{1}{\sqrt{1 + n\zeta^2}} \hat{U} \cdot \hat{e}_\lambda, \tag{3.64}
\]

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Figure 3.1: (a) Schematic plot of the value of the order parameter (brightness) at the stationary point, for two replicas labeled by $x^1$ and $x^2$. (b) Schematic plot of the value of the order parameter (brightness) for a Goldstone deformation of the stationary point, for two replicas labeled by $x^1$ and $x^2$. 
Figure 3.2: Example of a Goldstone deformed state. The system in replicas 0 through n are shown. The mean positions of the replicas of a thermally fluctuating particle are displaced to \((z, R^1(z), \ldots, R^n(z))\) in this Goldstone deformed state, which characterizes an \(n\)-fold replicated deformation field. Here for simplicity we only show spatially homogeneous deformations, and it is worth noticing that the volume of the measurement replicas, \(i.e., \) replicas 1 through \(n\), are contracted by a factor \(\zeta^d\).

by which \(\hat{y}_\lambda \equiv (y, \zeta y, \ldots, \zeta y) = \hat{x}_\lambda + \hat{U}_\lambda\). The Jacobian of this change of variables is unity, provided that each deformation \(z \rightarrow U^\alpha(z)\) is a pure shear deformation.

1With this change of variables the Goldstone-deformed order parameter becomes

\[
\Omega_{GS}(\hat{x}) = \frac{Q}{V_0} \int \frac{dy}{V_0} \int d\tau \mathcal{P}(\tau) \left( \frac{\tau}{2\pi} \right)^{(1+n)d} e^{-\frac{\tau}{2}(x_{\lambda} - \hat{y}_{\lambda})^2 - \frac{\tau}{2}(x_{\tau} - \hat{U}^\tau(y))^2} - \frac{Q}{V_0 V^n} \Omega_{GS}'(\hat{y})
\]

where the transformed deformation field is defined by \(\hat{U}^\tau(y) = \hat{U}_\tau(z)\). With this change of variables, the order parameter field is transformed to a new field, \(\Omega_{GS}'(\hat{y})\) of \(\hat{y}\), which can be viewed as translated purely in the \(\hat{x}_\tau\) direction from the stationary point \(\Omega_{SP}(\hat{y})\), because the deformation is \(\hat{R}(y) = \hat{y} + \hat{U}^\tau(y)\).

Comparing with the deformation before the change of variables, \(\hat{R}(z) = \hat{z} + \hat{U}(z)\), it is evident that the \(U_\lambda\) component is actually removed, and the deformation field \(\hat{U}\) only affects the \(\hat{x}_\tau\) direction. Therefore, \(U_\lambda\) is a redundant component in this field-theoretic description of the Goldstone mode. Note that in these two forms of the Goldstone mode, Eqs. (3.60) and (3.65), the number of degrees of freedom of the deformation field \(U(z)\) or \(\hat{U}^\tau(y)\), are \(nd\), as in \(U(z)\) one has the constraint \(U^0 = 0\).

The reason we choose to adopt the form of Goldstone mode (3.60) is that in the real physical system that we are intending to describe, the preparation state (replica 0) is not deformed. Although in the field theory the \(1+n\) replicas are present symmetrically (apart from the contraction \(\zeta\)), physically, one should only have Goldstone modes that deform replicas 1 through \(n\), as these are the replicas associated with the measurement ensembles, on which deformations are actually performed. Therefore, although Eqs. (3.60) and (3.65) are mathematically equivalent, only Eq. (3.60) describes the physically reasonable Goldstone

---

1This relation is correct to linear order in \(U\) or linear order in \(n\).
modes.

Secondly, in earlier works [56, 55], the form of the Goldstone deformation was written as

$$\Omega(\hat{x}) = Q \int d\tau P(\tau) \left( \frac{T}{2\pi} \right)^{1+n} e^{-\frac{T}{2} |\hat{x}_\tau - \hat{U}_\tau(x_\lambda)|^2} - \frac{Q}{V_0 V^n}$$ (3.66)

This form (we shall call it the “old Goldstone deformation”) differs from the Goldstone deformation we are currently using (“new Goldstone deformation”) in two ways: (1) In the old Goldstone deformation the deformation field is a function of $x_\lambda$ (and, as a result, $z$ can be integrated out as in the stationary-point form). However, in the new Goldstone deformation, the deformation is a function of $z$. The new Goldstone deformation is more physical, in the sense that the deformation field should be defined in terms of the mean positions $z$ during thermal fluctuations, not the instantaneous positions of the particles $\hat{x}$. In the new Goldstone deformation, it is clear that the mean positions are deformed, $\hat{z} \rightarrow \hat{R}(z)$, but the shape of the thermal cloud, which corresponds to a “massive” mode, is left untouched. (2) The deformation field in the old Goldstone deformation lies in the $\hat{x}_\tau$ direction, whereas the new Goldstone deformation has a deformation field in the replicas 1 through $n$. This has already been discussed above, as has been the point that they are related by a change of variables. The new Goldstone structure is more physical, in the sense that the preparation state (replica 0) cannot be deformed once the sample has been made.

### 3.4.3 Energetics of Goldstone deformations

We take the Goldstone-deformed order parameter, in its momentum-space form, to be

$$\langle \Omega_{GS} \rangle_{\hat{p}} = Q \int dz \int d\tau P(\tau) e^{-\frac{\hat{p}^2}{2\tau} - i\hat{p} \cdot \hat{R}(z)} - Q \delta^{(1+n)} d,$$ (3.67)

and insert it into the Hamiltonian (3.32). This calculation gives us the free energy of a deformed state, as in the calculation of the stationary-point free energy.

After a lengthy calculation (see Appendix E), we arrive at the energy of the Goldstone deformed state:

$$H_{\Omega_{GS}} = H_{\Omega_{SP}}^{(SP)} + H_{\Omega_{\Psi R}}.$$

Here, we use the shorthand $\Psi_R(z_1, z_2) \equiv (\hat{R}(z_1) - \hat{R}(z_2))^2 - (1 + n)(z_1 - z_2)^2$ to denote the deformation. $H_{\Omega_{SP}}^{(SP)}$ is the Hamiltonian for the stationary point, as given in Eq. (3.44), and the term $H_{\Omega_{\Psi R}}$ accounts for the increase in the energy.
due to Goldstone deformation, which is

\[
H_{\Omega}^{\Psi_R} = -Nk_BT \frac{\theta_d}{2} c^2 \int dz_1 dz_2 K_1(z_1, z_2) \Psi_R(z_1, z_2) \\
- \frac{1}{8k_BT} \int dz_1 dz_2 dz_3 dz_4 K_2(z_1, z_2, z_3, z_4) \Psi_R(z_1, z_2) \Psi_R(z_3, z_4),
\]

(3.69)

where the functions \( K_1(z_1, z_2) \) and \( K_2(z_1, z_2, z_3, z_4) \) are bell-shaped functions of the distances \((z_1 - z_2)\) and \((z_1 - z_2), (z_2 - z_3), (z_3 - z_4)\), as shown in Fig. 3.3. The fluctuations are independent of the centers of mass, \((z_1 + z_2)/2\) for \( K_1(z_1, z_2) \), and \((z_1 + z_2 + z_3 + z_4)/4\) for \( K_2(z_1, z_2, z_3, z_4) \). The forms of \( K_1(z_1, z_2) \) and \( K_2(z_1, z_2, z_3, z_4) \) are given in Appendix E.

\[
K_1(z_1, z_2) = \sum \begin{array}{c}
\bullet \\
\bullet
\end{array}
\]

\[
K_2(z_1, z_2, z_3, z_4) = \sum \begin{array}{c}
\bullet \\
\bullet
\end{array}
\]

\[
+ \sum \begin{array}{c}
\bullet \\
\bullet
\end{array}
\]

\[
+ \sum \begin{array}{c}
\bullet \\
\bullet
\end{array}
\]

Figure 3.3: Diagrams for the function \( K_1(z_1, z_2) \) and \( K_2(z_1, z_2, z_3, z_4) \). In these diagrams, the wavy lines represent Gaussian potentials between the two points on the scale of localization length, averaged over the probability distribution of localization length, represented by the summation in the diagrams. The straight lines represent delta functions. The full expression is listed in Appendix E.

Alternatively, in order to compare with the phenomenological elastic free energy that we shall discuss in Chapter 4, the energy of the Goldstone deformations can be written in the form

\[
H_{\Omega}^{(GS)} = H_{\Omega}^{(0)} + H_{\Omega}^{(R)}.
\]

(3.70)

In this form, we are separating the Hamiltonian into two parts. \( H_{\Omega}^{(0)} \) gives energy of the “state right after linking”, which is a state that has not been allowed to contract after the links were made, and thus has the same volume and shape as the liquid state. In the state right after linking, the mean positions of the replicas of the thermally fluctuating particle (i.e., the centers of the thermal cloud) are located at positions \((x_0, x_1, \ldots, x_n) = (z, z, \ldots, z)\). The other part of the Hamiltonian is the elastic energy of the deformation from this state, \( H_{\Omega}^{(R)} \). This is different from the separation in Eq. (3.68), in which one has the stationary point energy \( H_{\Omega}^{(SP)} \) and the energy increase due to Goldstone
deformations $H_{\Omega}^{\Psi_R}$. The relation between these two separations is given by

\begin{align}
H_{\Omega}^{(0)} &= H_{\Omega}^{(GS)} - h(\zeta), \\
H_{\Omega}^{(R)} &= H_{\Omega}^{\Psi_R} + h(\zeta),
\end{align}

(3.71)

where $h(\zeta)$ accounts for the energy of the stationary point, measured with respect to the state right after linking, which is actually the elastic energy of the contraction $\zeta$, i.e.,

$$h(\zeta) = \frac{\nu^2 N^2}{2V_0} \left( \frac{V}{V_0} - 1 \right)^2 + Nk_BT\frac{\theta d}{2}(\zeta^2 - 1).$$

(3.72)
Chapter 4

Phenomenological theory for the elasticity of soft random solids

4.1 Phenomenological nonlocal elastic free energy

As we discussed in Section 1.2.1, in the classical theory of rubber elasticity [6] rubbery materials are modeled as incompressible networks of entropic Gaussian chains, and the resulting elastic free energy density is given by

\[ f = \frac{\mu}{2} \text{Tr} \Lambda^T \Lambda \quad (4.1) \]

for uniform deformations \( r \rightarrow \Lambda \cdot r \). Incompressibility is incorporated via the constraint \( \det \Lambda = 1 \). For the shear modulus \( \mu \), the classical theory gives the result \( n_c k_B T \), where \( n_c \) is the density of effective chains in the network.

The phenomenological model that we now discuss is in the spirit of the classical theory of rubber elasticity. However, to account for the heterogeneity of the medium, we need to introduce the additional feature of quenched randomness into the model, and thus the entropic Gaussian chains are of heterogeneous length and density.

Inspired by the form of the energy of Goldstone fluctuations determined from the RLPM in Section 3.4.3, we choose the following elastic free energy \( \Gamma \) associated with a deformation \( R(z) \) of the soft random solid state that maps the mass point at \( z \) to the new location \( R(z) \):

\[ \Gamma = \frac{1}{2} \int \! dz_1 \! dz_2 \, G(z_1, z_2) \left( |R(z_1) - R(z_2)|^2 - |z_1 - z_2|^2 \right) \]

\[ + \frac{\lambda_0}{2} \int \! dz \left\{ \det \left( \frac{\partial R_i(z)}{\partial z_j} \right) - 1 \right\}^2, \quad (4.2) \]

where \( G(z_1, z_2) \) is a nonlocal harmonic attraction that serves to pull the two “mass points” (i.e., coarse-grained volume-elements) at \( z_1 \) and \( z_2 \) toward one another. \( G(z_1, z_2) \) originates in the entropy of the molecular chains of the heterogeneous network, and we model it as “zero rest-length” springs having random spring coefficients. Notice that \( G(z_1, z_2) \) is a coarse grained consequence of many molecular chains and, more importantly, is an entropic effect and does not depend on the choice of precise form of microscopic attractive interactions.
WE take the kernel $G(z_1, z_2)$ to be a quenched random function of the two positions, $z_1$ and $z_2$, symmetric under $z_1 \leftrightarrow z_2$. We assume that the disorder average of $G(z_1, z_2)$ is $G(0)(z_1 - z_2) \equiv [G(z_1, z_2)]$, i.e., is translationally invariant. Furthermore, we define the fluctuation part of $G(z_1, z_2)$ to be $G(1)(z_1, z_2) \equiv G(z_1, z_2) - G(0)(z_1 - z_2)$. In the following analysis, we assume that $G(1) \ll G(0)$ in order to make a necessary perturbative expansion.

In the second term in Eq. (4.2), the determinant of the deformation gradient tensor $\Lambda_{ij}(z) \equiv \partial R_i / \partial z_j$ captures the change of the volume and, correspondingly, the parameter $\lambda_0$, which we take to be large, heavily penalizes density variations. This large $\lambda_0$ results from a competition between (i) repulsions (either direct or mediated via a solvent, e.g., excluded volume), and (ii) intermolecular attractions and external pressure.

In discussion of elasticity that follows, we introduce the notion of “reference space” and a “target space” for any deformation $R(z)$. The reference space, labeled by the $d$-dimensional vector $z$, is the space before the deformation, whereas the target space, labeled by the $d$-dimensional vector $R(z)$, is the space after the deformation.

4.2 Relaxation for a given realization of disorder

The free energy $\Gamma$ provides a natural description of the heterogeneous elasticity of soft random solids. However, the stable state is not $R(z) = z$ (i.e., the state $R(z) = z$ does not satisfy the stationarity condition $\delta I / \delta R(z) = 0$). There are two reasons for this instability. First, the attraction $G$ causes a small, spatially uniform contraction [the fractional volume change being $O(1/\lambda_0)$]. Second, the randomness of $G$ additionally destabilizes this contracted state, causing the adoption of a randomly deformed stable state. We denote this relaxation as $z \rightarrow \tilde{z} \equiv \zeta z + v(z)$, in which $\zeta$ describes the uniform contraction and $v(z)$ describes the random local deformation. This relaxation process can be understood in the setting of the preparation of a sample of rubber via instantaneous crosslinking: crosslinking not only drives the liquid-to-random solid transition but it also generates a uniform inward pressure, as well as introducing random stresses, as shown in Fig. 4.1. As a result, immediately after crosslinking the state is not stable, but relaxes to a new stable state, determined by the particular realization of randomness created by the crosslinking. In the following discussion, we shall name the state $R(z) = z$ the “state right after linking”, and the state $R(z) = \tilde{z} \equiv \zeta z + v(z)$ as the “relaxed state”. The state right after linking, here, is the same as the one just defined below Eq. (3.70), which has the energy $H^{(0)}(\Omega)$ in RLPM, because they both describe the state that has undergone no deformation since being linked.

By writing the relaxation as $z \rightarrow \tilde{z} = \zeta z + v(z)$ we are making the approxi-
Figure 4.1: Schematic plot of the relaxation process under a fixed pressure. (a) The liquid state with no linking. (b) The state right after linking. Crosslinks are added to the system, and an infinite cluster is formed. This state is not stable, because of the inward pressure and local stresses. (c) The relaxed state. The system undergoes a uniform contraction and random local deformations that release the unbalanced stress introduced by crosslinking.

imation that the contraction $\zeta$ is homogeneous and the random deformations $v(z)$ are pure shear, which means that any randomness in the bulk deformation is ignored. This can be understood by looking at the orders of magnitude of the deformations. The uniform contraction is of order $O(G^{(0)}/\lambda_0)$, and the random local shear deformations are of order $O(G^{(1)}/G^{(0)})$. The random local bulk deformations is, however, of order $O(G^{(1)}/\lambda_0)$, and is thus much smaller than the other two deformations, given the assumption that the fluctuations of the shear modulus are much smaller than the mean (the shear modulus corresponds to $G$, as we shall see later), and the shear modulus is much smaller than the bulk modulus.

With these assumptions, we can insert the form $R(z) = \vec{z} = \zeta z + v(z)$ into the stationarity condition, and solve for the relaxed state, which is characterized by $\zeta$ and $v(z)$. As we have just discussed, for the contraction, only the homogeneous part is considered, so the variational equation for $\zeta$ assumes $G^{(1)} = 0$ and thus $v(z) = 0$, and so stationarity requires

$$\frac{\partial \Gamma}{\partial \zeta} = 0. \tag{4.3}$$

Thus, for the present model, Eq. (4.2), we have

$$0 = \frac{\partial}{\partial \zeta} \left\{ \frac{1}{2} \int dz_1 dz_2 G^{(0)}(z_1, z_2)(\zeta^2 - 1)|z_1 - z_2|^2 + \frac{\lambda_0}{2} \int dz(\zeta^d - 1)^2 \right\} = V_0(\rho \zeta^d + \lambda_0(\zeta^d - 1)d\zeta^{d-1}). \tag{4.4}$$

By solving this equation to leading order in $\rho/\lambda_0$, we obtain

$$\zeta \approx 1 - (\rho/d\lambda_0), \tag{4.5}$$

where

$$\rho \equiv \frac{1}{d} \int dz_2 (z_1 - z_2)^2 G^{(0)}(z_1 - z_2). \tag{4.6}$$
As we shall see below, $\rho$ is actually the mean shear modulus.

The stationarity condition for the random local deformations $v(z)$ is

$$\frac{\delta \Gamma}{\delta v_a(z)} = 0, \quad (4.7)$$

and for the present model, Eq. (4.2), this condition reads

$$2(\zeta z_a + v_a(z)) \int dz_2 G(z, z_2) - 2 \int dz_2 G(z, z_2)(\zeta z_{a,2} + v_a(z_2)) - \lambda'_0 \partial_a \left( \partial_i v_i(z) \right) = 0. \quad (4.8)$$

Here, the last term, $\lambda'_0 \partial_a \left( \partial_i v_i(z) \right)$ is associated with a density variation, and arises from the variation of the second term in the elastic free energy (4.2), which is $\lambda_0 \int dz \left\{ \det \left( \partial R_i(z)/\partial z_j \right) - 1 \right\}^2$. (In the following discussion we shall call this the “bulk term” in the elastic free energy), and we have made the definition $\lambda'_0 \equiv \zeta^{2d-2} \lambda_0$; see Appendix F for the expansion.

The stationarity equation (4.8) for $v(z)$ can be solved perturbatively by assuming that $G^{(0)}$ is of zeroth order and that $G^{(1)}$ and $v(z)$ are of first order; see Appendix F for the calculation. In momentum-space, the result is

$$\vec{v}_p = \frac{\vec{p}^T \cdot \vec{f}_p}{2D_p} + \frac{\vec{p}^L \cdot \vec{f}_p}{\lambda'_0 |p|^2 + 2D_p}, \quad (4.9)$$

where $p$ is the $d$-dimensional momentum vector. The notation $\vec{f}_p$, $D_p$ are given in Appendix F. The definitions of the projection operators $\vec{p}^L$ and $\vec{p}^T$ are defined as,

$$p^L_{ij} \equiv p_i p_j / p^2,$$

$$p^T_{ij} \equiv \delta_{i,j} - p_i p_j / p^2. \quad (4.10)$$

We use bold letters to denote $d$-dimensional rank-2 tensors, and add an overhead arrow [such as $\vec{v}$] to denote vectors, when needed.

### 4.3 Elastic free energy expanded around the relaxed state

In order to obtain a description of the elasticity of the relaxed state, which is stable and thus relevant for experimental observations, we re-expand the phenomenological elastic free energy (4.2) around the relaxed state $\tilde{z}$. This amounts to taking the relaxed state $\tilde{z} \equiv \zeta z + v(z)$ as the new reference state, and deriving the elastic free energy for deformations relative to this state.

To do this, we study the free energy for the following elastic deformation:

$$z \rightarrow R(z) = \tilde{z} + u(z) \quad (4.11)$$

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where $u(z)$ is a deformation away from the relaxed state. We make the following change of variables $z \to \tilde{z}(z)$:

$$z \to \tilde{z} \equiv \zeta z + v(z), \quad (4.12)$$

which has the Jacobian factor

$$J(z) \equiv \left| \frac{\partial \tilde{z}_i}{\partial z_j} \right| \simeq \zeta^d \left( 1 + \zeta^{-1} \partial_j v_j(z) \right). \quad (4.13)$$

With this change of variables, the free energy is expressed as

$$\Gamma = \Gamma_0 + \frac{1}{2} \int d\tilde{z}_1 d\tilde{z}_2 J(z_1)^{-1} J(z_2)^{-1} \tilde{G}(\tilde{z}_1, \tilde{z}_2) \times \left( |\tilde{z}_1 + \tilde{u}(\tilde{z}_1) - \tilde{z}_2 - \tilde{u}(\tilde{z}_2)|^2 - |\tilde{z}_1 - \tilde{z}_2|^2 \right)$$

$$+ \frac{\lambda_0}{2} \int d\tilde{z} J(z)^{-1} \left( J(z) \det \left( \frac{\partial \tilde{z}_i + \tilde{u}_i(\tilde{z})}{\partial \tilde{z}_j} \right) - 1 \right)^2, \quad (4.14)$$

where we have made the definitions

$$\tilde{G}(\tilde{z}_1, \tilde{z}_2) \equiv G(z(\tilde{z}_1), z(\tilde{z}_2)), \quad (4.15a)$$

$$\tilde{u}(\tilde{z}) \equiv u(z(\tilde{z})), \quad (4.15b)$$

$$\tilde{R}(\tilde{z}) \equiv \tilde{z} + \tilde{u}(\tilde{z}), \quad (4.15c)$$

with $z(\tilde{z})$ denoting the mapping of the mass point $\tilde{z}$ in relaxed state back to the mass point $z$ in the state right after linking, i.e., the inverse of the $\tilde{z}(z)$ mapping. The change of the free energy due to a different reference state is defined as $\Gamma_0$ is defined as $\Gamma_0 \equiv \frac{1}{2} \int d\tilde{z}_1 d\tilde{z}_2 G(z_1, z_2)(|\tilde{z}_1 - \tilde{z}_2|^2 - |z_1 - z_2|^2)$, which is a constant for a given realization of the randomness.

In order to obtain a direct description of the elastic energy relative to the relaxed state, we expand the quenched random nonlocal kernel in the relaxed state, $\tilde{G}(\tilde{z}_1, \tilde{z}_2)$, defined in Eq. (4.15a), for $G^{(1)} \ll G$. This calculation is given in Appendix G.1, and in momentum space the result is

$$\tilde{G}_{\tilde{p}_1, \tilde{p}_2} \simeq G^{(0)}_{\tilde{p}_1, \tilde{p}_2} + G^{(1)}_{\tilde{p}_1, \tilde{p}_2} - i \left( \tilde{p}_1 \cdot \tilde{v}_{\tilde{p}_1 + \tilde{p}_2} G^{(0)}_{\tilde{p}_2} + \tilde{p}_2 \cdot \tilde{v}_{\tilde{p}_1 + \tilde{p}_2} G^{(0)}_{\tilde{p}_1} \right), \quad (4.16)$$

where $\tilde{v}$ is the random local deformation field defined in Section 4.2, and is related to $G$ via Eq. (4.9). In this expansion, $\tilde{G}$ is directly expressed in terms of $G$.

We then expand the elastic free energy as a power series in the small deformation $\tilde{u}(\tilde{z})$ away from the relaxed state $\tilde{z}$. The calculation of this expansion is given in Appendix G.

As we shall show in Chapter 5, the statistics of the quenched randomness in this phenomenological theory can be determined via a comparison with the RLPM. Through this comparison, we found that, the lengthscale of the nonlocal
kernel $G$ is actually the typical localization length, which is small compared to the lengthscales on which our theory of elasticity applies, because the deformations in this theory are associated with Goldstone fluctuations in the RLPM, which feature lengthscales much larger than the typical localization length.

Thus, it is reasonable to make a local expansion of the elastic energy relative to the relaxed state, and obtain a local form of elasticity, in terms of the strain tensor $\epsilon$. The resulting form of the elastic free energy, which we shall call “the local form of the elastic energy relative to the relaxed state”, is in the form of Lagrangian elasticity, (which is introduced in Section 1.2).

The advantage of this local form of the elastic energy, as will be seen in Section 5.3, is that one can extract the large-distance behaviors of the correlators of the elastic parameters, which turn out to be universal.

and this continuous description can be obtained by making a local expansion on the nonlocal term in (4.14).

The calculation for this local expansion is given in Appendix G, and the resulting local form of elastic energy is

$$
\Gamma = \int d\tilde{z} \left\{ \text{Tr}(\sigma(\tilde{z}) \cdot \tilde{\epsilon}(\tilde{z})) + \mu(\tilde{z})\text{Tr}\tilde{\epsilon}(\tilde{z})^2 + \frac{\lambda(\tilde{z})}{2} (\text{Tr}\tilde{\epsilon}(\tilde{z}))^2 \right\},
$$

(4.17)

where the strain tensor relative to the relaxed state is defined as

$$
\tilde{\epsilon}_{ij} \equiv \frac{1}{2} \left( \frac{\partial \tilde{u}_j}{\partial \tilde{z}_i} + \frac{\partial \tilde{u}_i}{\partial \tilde{z}_j} \right),
$$

(4.18)

and the heterogeneous elastic parameters, namely the residual stress $\sigma$, the shear modulus $\mu$, and the bulk modulus $\lambda$, are given in momentum space, by

$$
\sigma_{ij,\tilde{p}} = -\frac{\partial^2}{\partial \tilde{q}_i \partial \tilde{q}_j} \left|_{\tilde{q}=0} \right. G_{\tilde{p}-\tilde{q},\tilde{p}}^{(1)} + i\delta_{ij} \left( \frac{\tilde{p} \cdot \tilde{f}_{\tilde{p}}}{|\tilde{p}|^2} - \frac{f_{a,\tilde{p}a,\tilde{p}}^{T} + \tilde{p}_a \tilde{p}_a^{T}}{2} \right),
$$

(4.19a)

$$
\mu_{\tilde{p}} = \rho V_{0} \delta_{\tilde{p}} - \frac{\tilde{p} \cdot \tilde{f}_{\tilde{p}}}{|\tilde{p}|^2},
$$

(4.19b)

$$
\lambda_{\tilde{p}} = \lambda_{0} V_{0} \delta_{\tilde{p}} + 2 \left\{ \frac{i\tilde{p} \cdot \tilde{f}_{\tilde{p}}}{|\tilde{p}|^2} - \rho V_{0} \delta_{\tilde{p}} \right\},
$$

(4.19c)

where in the expression for $\sigma_{ij,\tilde{p}}$ we have only kept terms to leading order in the momentum $\tilde{p}$ (see Appendix G for the derivation). It is worth mentioning that, to leading order in the momentum $\tilde{p}$, this residual stress satisfies the stability condition $\tilde{p}_a \sigma_{ij,\tilde{p}} = 0$, because the reference state of this elastic free energy, the relaxed state, is a stable state. This will also be shown more directly in the final results in Section 5.3.

\(^1\)To be consistent with the RLPM, we have used finite-volume versions of the Fourier transform and Kronecker delta function in momentum space; we shall take the continuum limit later, in the final results in Section 5.3.2. Strictly speaking, the differentiations in Eq. (4.19a) should be understood as difference quotients instead.
4.4 Nonaffine deformations for a given realization of disorder

Because of the quenched disorder present in the elastic parameter $G$ of our phenomenological model, Eq. (4.2), upon the application of external stress, the system will respond by adopting a strain field that is nonaffine (i.e., characterized by a strain tensor that is inhomogeneous in space). Such non-affine deformations reflect the quenched randomness in the elasticity, and can be derived for a given realization of disorder and a given macroscopic deformation by external stress. Because the deformation is the quantity that is directly measurable in experiments, it is useful to derive the relationship between the nonaffine deformations and the quenched randomness in the elastic parameters. Then, by comparing with the RLPM, we shall obtain a statical description of the nonaffine deformations, as in Section 5.4.

To study nonaffine deformations, it is convenient to take the “state right after linking” [i.e., the state $R(z) = z$ as in Eq. (4.2)] as the reference state, and to re-derive the relaxation in presence of a given deformation $\Lambda$. This is equivalent to applying the deformation $\Lambda$ to the relaxed state, and then letting the system further relax for this given deformation, as shown in Fig. 4.2. The relaxed state for this given deformation $\Lambda$, which we term the “relaxed deformed state”, is described by the deformation $z \rightarrow \tilde{z}_{\Lambda}(z)$. We suppose that

$$\tilde{z}_{\Lambda}(z) = \zeta \cdot z + v_{\Lambda}(z).$$  \hspace{1cm} (4.20)

For simplicity, we assume that the deformation $\Lambda$ is pure shear (i.e., $\det \Lambda = 1$).

Next, we use the two stationarity conditions, Eqs. (4.3, 4.7) to solve for the relaxed deformed state. The stationarity equation (4.4) for the homogeneous contraction $\zeta$, is unchanged, so we still have $\zeta \approx 1 - (\rho/d\lambda_0)$. For the stability equation for the random local deformations $v_{\Lambda}$, we follow a similar expansion to the one in Eqs. (F.1) and (F.2), arriving at

$$2(\zeta_{\Lambda}a z_i + (v_{\Lambda})_a(z)) \int dz_2 G(z, z_2)$$
$$-2 \int dz_2 G(z, z_2)(\zeta_{\Lambda}a z_2,i + (v_{\Lambda})_a(z_2)) - \lambda_0^{-1} \lambda_0^{-1} \partial_i \partial_j (v_{\Lambda})_a(z) = 0. \hspace{1cm} (4.21)$$

As with the derivation given in Section 4.2, we can solve this equation perturbatively, to leading order in $G^{(1)}$ and $v_{\Lambda}$; see Appendix H for details. The result is

$$(v_{\Lambda})_p = \left\{ \frac{p_T}{2D_p} + \frac{p_L}{\lambda_0|p|^2 + 2D_p} \right\} \cdot (f_{\Lambda})_p, \hspace{1cm} (4.22)$$

where $p_T$ and $p_L$, defined in Appendix H, are the deformed versions of the projection operators.
in the literature the nonaffine deformations are often characterized by the "nonaffine deformation field" $w_\Lambda$, which is defined in momentum-space as

$$
(w_\Lambda)_p \equiv \Lambda^{-1} \cdot (\tilde{z}_\Lambda)_p = \Lambda^{-1} \cdot (v_\Lambda)_p - v_p,
$$

(4.23)

where $\tilde{z}$ denotes the relaxed state of the undeformed system (as discussed in Section 4.2), and $\tilde{z}_\Lambda$ is the relaxed deformed state.

Inserting the solution of $v_\Lambda$ into the expression for nonaffine deformation field, Eq. (4.23), we have

$$
(w_\Lambda)_p = 2\iota \left\{ \frac{\lambda'_0 |p|^2}{(\lambda'_0 |p|^2 + 2D_p)2D_p} g^{-1} - \frac{\lambda'_0 |p|^2}{(\lambda'_0 |p|^2 + 2D_p)2D_p} \frac{1}{D_p} \right\} \cdot p^L \cdot S_p,
$$

(4.24)

where

$$
S_p \equiv \frac{\partial}{\partial p_{1,a}} G^{(1)}_{p_{1,0}} - \frac{\partial}{\partial p_{2,a}} \bigg|_{p_2=0} G^{(1)}_{p_{2,0}},
$$

(4.25)

and

$$
g = \Lambda^T \Lambda.
$$

(4.26)
\[(w_\Lambda)_p \simeq \frac{1}{2D_p t_1} \mathbf{g}^{-1} - \frac{1}{2D_p} \mathbf{1} \cdot \mathbf{p}^L \cdot \mathbf{S}_p.\]  

(4.27)

4.5 Disorder average of the phenomenological model via replica method

To make a comparison with the RLPM, and thus to obtain information about the statistics of the nonlocal kernel \(G\) that characterizes the disorder present in the phenomenological model, we shall use the replica method to calculate the elastic free energy of the phenomenological model, averaged over some as-yet unspecified distribution of quenched disorder.

We follow a recipe similar to the one used in Section 3.1 [see Eq. (3.9)]. The elastic free energy, Eq. (4.2), contains the random ingredient \(G\). As with the RLPM, the physical quantity to be disorder-averaged is the free energy at a given pressure, but now with the deformations \(R(z)\) as thermally fluctuating field. Therefore we need to take \(\Gamma\), defined in Eq. (4.2), as the effective Hamiltonian, because it is the elastic energy for a given deformation field specified by \(R(z)\), and then calculate the free energy at a given temperature, via the partition function

\[Z_G = \int DRe^{-\Gamma_G(R(z))/k_BT},\]  

(4.28)

with \(\Gamma\) depending on the quenched randomness through its nonlocal kernel \(G\). The Gibbs free energy is related to this partition function via \(\mathcal{G} = -k_BT \ln Z\), and \(\mathcal{G}\) is the quantity that should be averaged over the quenched disorder. Note that it is the Gibbs free energy, instead of Helmholtz free energy, that is related to this partition function \(Z\), because in the elastic energy \(\Gamma\) one has a fixed pressure, which is accounted for by the bulk term, the volume being allowed to fluctuate. The disorder average of the Gibbs free energy can be completed using the replica technique:

\[
\mathbb{G} = -k_BT \int DG \mathcal{P}_G \ln Z_G
\]

\[
\mathbb{G} = -k_BT \int DG \mathcal{P}_G \lim_{n \to 0} \frac{Z_G^n - 1}{n}
\]

\[
\mathbb{G} = -k_BT \lim_{n \to 0} \frac{\partial}{\partial n} \bigg|_{n=0} [Z_G^n],
\]  

(4.29)

where we have used \([\cdots] \equiv \int DG \mathcal{P}_G \cdots\) once again to denote a disorder average but this time over the values of the quenched random kernel \(G\), weighted by an as-yet unknown distribution \(\mathcal{P}_G\). In the present setting we do not have a “zeroth replica”, as such a replica arises from the Deam-Edwards distribution of the links, and this is not the type of quenched disorder that we have in
mind. Rather, in the present setting we regard the distribution of disorder $\mathcal{P}_G$ as a physical quantity that is unknown but is to be determined through a comparison with the analysis of the Goldstone fluctuations of the RLPM. The replica partition function is then given by

$$Z_n = [Z^n_G] = \int \mathcal{D}G \mathcal{P}_G Z^n_G = \int \mathcal{D}G \mathcal{P}_G \prod_{\alpha=1}^n \mathcal{D}R^\alpha e^{-\sum_{\alpha=1}^n \Gamma_G(R^\alpha(z))/k_B T} = \int \prod_{\alpha=1}^n \mathcal{D}R^\alpha e^{-\Gamma_n/k_B T},$$

where we are functionally integrating over the configurations of the $n$-fold replicated displacement fields: $R^\alpha$. We have also introduced the effective, pure Hamiltonian $\Gamma_n$ that governs the replicated deformation fields

$$\Gamma_n \equiv -k_B T \ln [e^{-\sum_{\alpha=1}^n \Gamma_G(R^\alpha(z))/k_B T}].$$

where $[\cdots]$ denote disorder average weighted by $\mathcal{P}_G$. The exponential and the logarithm function in Eq. (4.31) can jointly be expanded via the cumulant expansion, and thus we arrive at the form

$$\Gamma_n = -k_B T \left\{ -\left[ \sum_{\alpha=1}^n \Gamma_G(R^\alpha(z))/k_B T \right]_c + \frac{1}{2} \left[ \sum_{\alpha,\beta=1}^n \Gamma_G(R^\alpha(z))\Gamma_G(R^\beta(z))/k_B T \right]_c - \cdots \right\},$$

where $[\cdots]_c$ are connected statistical moments (cumulants) given the probability distribution of the disorder $\mathcal{P}_G$, and the omitted terms are $O((\Gamma/k_B T)^3)$. The elastic energy for a given realization of disorder $G$ and a given deformation field $R(z)$ is given in Eq. (4.2); inserting this form we have

$$\Gamma_n = \frac{\lambda_0}{2} \int \prod_{\alpha=1}^n (|\partial R^\alpha| - 1)^2 + \frac{1}{2} \int_{z_1, z_2} [G(z_1, z_2)]_c \Psi_R(z_1, z_2)$$

$$- \frac{1}{8k_B T} \int_{z_1, z_2, z_3, z_4} [G(z_1, z_2)G(z_3, z_4)]_c \Psi_R(z_1, z_2)\Psi_R(z_3, z_4) + O(\Psi_R^3),$$

where we remind the reader of the definition of $\Psi_R$, first given in Section 3.4.3:

$$\Psi_R \equiv (\hat{R}(z_1) - \hat{R}(z_2))^2 - (1 + n)(z_1 - z_2)^2.$$

This effective, pure Hamiltonian $\Gamma_n$ has precisely the same form as the energy of the Goldstone fluctuations (3.69), derived microscopically from the RLPM.
Thus, the RLPM actually provides a *derivation* of the phenomenological model we proposed in Section 4.1, and *justifies*, from a microscopic perspective, the phenomenological elastic free energy (4.2) with its quenched randomness. Therefore, the probability distribution $P_G$ of the quenched randomness in Eq. (4.2) is contained in the RLPM. By comparing the two schemes, *i.e.*, Eqs. (3.69) and (4.33), we arrive at a statistical description of the quenched random elastic parameters in the phenomenological model, as we shall show in Chapter 5.
Chapter 5

Determining the elastic quenched disorder

5.1 Comparing the Gibbs free energies of the randomly linked particle and phenomenological models

The RLPM is a semi-microscopic random network model, our analysis of which led to the disorder-averaged Gibbs free energy (3.12, 3.17):

\[
\mathcal{G} = -k_B T \lim_{n \to 0} \frac{\partial}{\partial n} \ln Z_{1+n} + pV, \quad (5.1)
\]

with

\[
Z_{1+n} = \int \mathcal{D} \Omega e^{-\frac{m}{n}}. \quad (5.2)
\]

The functional integration here is over all possible configuration of the order-parameter field $\Omega$. By contrast, in the phenomenological model, the replicated partition function $Z_n$ involves a functional integration over the $n$-fold replicated deformation field $R^a$, as in Eq. (4.30). The equivalence between the RLPM and the phenomenological model is revealed by noting that, in the random solid state, the Boltzmann weight in Eq. (5.2), $e^{-\frac{H}{k_B T}}$, only acquires considerable value at the stationary point $\Omega_{SP}$ and the Goldstone deformed states $\Omega_{GS}$, and decreases steeply for other sectors of fluctuations. This enables us to make the following approximation (up to a multiplicative constant from the Jacobian factor associated with the change of functional integration variables)

\[
Z_{1+n} \approx e^{-\frac{H^{(SP)}}{k_B T}} \int \mathcal{D} R e^{-\frac{H^{(GS)}}{k_B T}}, \quad (5.3)
\]

with $H^{(SP)}_\Omega$ and $H^{(GS)}_\Omega$ given in Eqs. (3.44) and (3.69).

In our phenomenological model, introduced in Section 4.1, the disorder-averaged Gibbs free energy is given by

\[
\mathcal{G} = -k_B T \lim_{n \to 0} \frac{\partial}{\partial n} \ln Z_n \quad (5.4)
\]
with
\[
Z_n = \int \mathcal{D}Re^{-\Gamma_n/k_BT}
\]
(5.5)
where $\Gamma_n$ is given in Eq. (4.33).

The Gibbs free energies, for the RLPM, and for the phenomenological model, are supposed to be equal, up to an additive constant, because they both capture the Gibbs free energy of a soft random solid system with elastic deformations. It is this equality that we shall now exploit to characterize, via the RLPM, the distribution of quenched disorder $P_G$ in the phenomenological model. Actually, we can directly identify the Hamiltonian $\Gamma_n$ with $H^{GS}(\Omega)$, because the functional integrations over the replicated deformation fields $R^{\alpha}$ are common to both the RLPM and the phenomenological model, in the sense that the deformation $z \rightarrow R^{\alpha}(z)$, in both the RLPM and the phenomenological model, takes the state right after linking as the reference state. Therefore, we have the relation
\[
\Gamma_n = H^{(R)}_{\Omega}.
\]
(5.6)
Notice that, here, the RLPM Hamiltonian is $H^{(R)}_{\Omega}$, not $H^{\Phi R}_{\Omega}$, because it is $H^{(R)}_{\Omega}$ that is the energy measured from the state right after linking, which matches the definition of reference state in the phenomenological theory, whereas $H^{\Phi R}_{\Omega}$ is the energy measured from the stationary point, which differs from the state right after linking by the energy of associated with the contraction $h(\zeta)$, given in Eq. (3.72).

By the comparison Eq. (5.6), we arrive at the following determination of the quenched-disorder characteristics of the phenomenological model (LHS) in terms of the elastic properties of the RLPM (RHS):
\[
[G(z_1, z_2)]_c = K_1(z_1, z_2),
\]
(5.7a)
\[
[G(z_1, z_2)G(z_3, z_4)]_c = K_2(z_1, z_2, z_3, z_4),
\]
(5.7b)
\[
\lambda_0 = \nu^2 n_0^2,
\]
(5.7c)
where $n_0 \equiv N/V_0$ is the number-density of the particles in the preparation state. The functions $K_1(z_1, z_2)$ and $K_2(z_1, z_2, z_3, z_4)$ are defined in Appendix E. Essentially, $K_1(z_1, z_2)$ is a Gaussian shaped function of the separation $|z_1 - z_2|$, averaged over distribution of localization lengths. The four-point function $K_2(z_1, z_2, z_3, z_4)$ has a combination of Gaussian and delta-function factors in the separations of the six pairs formed by the four points $\{z_1, z_2, z_3, z_4\}$. It is shown in Figure 3.3.
5.2 Disorder averages of the elastic parameters

In this section we shall determine the disorder averages of the position-dependent elastic parameters that characterize the elastic energy relative to the relaxed state. These elastic parameters, including the nonlocal kernel $\tilde{G}$, the residual stress $\sigma$, and the Lamé coefficients $\mu$ and $\lambda$, are determined for any particular realization of the elastic parameters $G$ and $\lambda_0$, as shown in Section 4.3. Thus, the elastic parameters of the heterogeneous elasticity relative to the relaxed state may be described via the statistical characterization of the quenched random parameters $G$ and $\lambda_0$ that we have just obtained; see Eqs. (5.7).

First, we determine the disorder average of the nonlocal kernel in the relaxed state $\tilde{G}$. To do this, we note that the nonlocal kernel of the relaxed state, $\tilde{G}$, is related to $G$ via Eq. (4.15a); the leading-order expansion of this relationship is given in Eq. (4.16). By taking the disorder average on both sides of Eq. (4.16), we find that only the first terms on the RHS survives, because other terms are all linear to the fluctuation part of $G$ and this vanishes upon disorder–averaging. Thus we find that the disorder average of $\tilde{G}$ is given by

$$[\tilde{G}(z_1, z_2)] = [G(z_1, z_2)] = K_1(z_1, z_2),$$

which means that the disorder average of $\tilde{G}$ is the same as the disorder average of $G$. It is worth noting that, as expected, because $K_1(z_1, z_2)$ is independent of the center of mass $\frac{1}{2}(z_1 + z_2)$ coordinates, the disorder average of the nonlocal kernel $[\tilde{G}(z_1, z_2)]$ is translational invariant, depending only on $|z_1 - z_2|$. This is a consequence of the macroscopic translational and rotational invariance of the random solid state discussed in Section 3.4.1.

Second, we determine the disorder averages of the position dependent elastic parameters in the local form of the elastic energy relative to the relaxed state, including the residual stress $\sigma$, the shear modulus $\mu$, and the bulk modulus $\lambda$. These elastic parameters are related to $G$ and $\lambda_0$ via Eqs. (4.19) for any given realization of disorder. Thus, as with the nonlocal kernel, we obtain the disorder averages of these elastic parameters, via the statistics of $G$.

The disorder average of the residual stress $\sigma$ is straightforwardly seen to vanish:

$$[\sigma_{ij}(z)] = 0.$$

Thus, the residual stress is a quenched random field with zero mean. As for the shear modulus $\mu$, its disorder average is given by

$$[\mu(z)] = \rho = -\frac{1}{d} \int d|z_2| \int d|z_2| |z-z_2|^2 = n_0 k_B T \theta,$$

with $\theta$ given in Eq. (3.45). This mean shear modulus is linear in temperature $T$, reflecting its entropic nature, a result that confirms this aspect of the classical
theory of rubber elasticity. As for the disorder average of bulk modulus $\lambda$, it is obtained via Eq. (5.7c), which gives

$$[\lambda(z)] = \nu^2 n_0^2.$$  \hfill (5.11)

As one might expect, the mean bulk modulus depends on the particle number density $n_0$ and the strength of the excluded volume interaction $\nu^2$. The disorder average of the three elastic parameters of the local form of the elastic energy relative to the relaxed state, $[\sigma_{ij}(z)], [\mu(z)],$ and $[\lambda(z)]$, are spatially all homogeneous and isotropic in space; this is also a result of the macroscopic translational and rotational invariance of the random solid state as discussed in Section 3.4.1.

5.3 Spatial correlations of the quenched random elastic parameters

5.3.1 Disorder correlator of the nonlocal kernel

The nonlocal kernel $\tilde{G}$ characterizes the quenched random nonlocal interactions in the relaxed state. The statistics of $\tilde{G}$ can be described via its statistical moments. In Section 5.2, we already determined the disorder average of $\tilde{G}$; in the present section we determine the disorder correlator of $\tilde{G}$.

To do this, we use Eq. (4.16), which relates $\tilde{G}$ to any given random configuration of $G$. Using the disorder correlator of $G$, Eq. (5.7b), we then arrive at the disorder correlator of $\tilde{G}$. The resulting disorder correlator, $[\tilde{G}(\tilde{z}_1, \tilde{z}_2)\tilde{G}(\tilde{z}_3, \tilde{z}_4)]$, is a combination of Gaussian and delta-function factors in the separations of the six pairs formed by the four points $\{\tilde{z}_1, \tilde{z}_2, \tilde{z}_3, \tilde{z}_4\}$. The derivation and the momentum-space expression of the result for this disorder correlator is given in Appendix I.1.

The universal characteristics of $[\tilde{G}(\tilde{z}_1, \tilde{z}_2)\tilde{G}(\tilde{z}_3, \tilde{z}_4)]$ are revealed by investigating its large-distance behavior, i.e., with the two pairs $\{\tilde{z}_1, \tilde{z}_2\}$ and $\{\tilde{z}_3, \tilde{z}_4\}$ far apart, but keeping $\tilde{z}_1$ near $\tilde{z}_2$, and $\tilde{z}_3$ near $\tilde{z}_4$, because $\tilde{G}(\tilde{z}_1, \tilde{z}_2)$ describes a short-distance attraction characterized by the scale of the typical localization length. This is the major reason for adopting the local description of elasticity, introduced in Section 4.3. This large-distance behavior is analyzed by deriving the correlations of the elastic parameters in the local form of the elastic energy relative to the relaxed state, as we shall now discuss.

5.3.2 Disorder correlators of the elastic parameters in the local form of the elastic energy

As already discussed in Section 5.3.1, one can extract the large-distance behavior of the disorder correlators of the heterogeneous elasticity in the relaxed state,
via the local form of the elastic energy. The elastic parameters in the local form of the elastic energy, including the residual stress $\sigma$, the shear modulus $\mu$, and the bulk modulus $\lambda$, are related to any given configuration $G$ via Eq. (4.19). Using these relations and the disorder correlator of $G$, Eqs. (5.7b), we arrive at the disorder correlators of the elastic parameters. The details of this calculation are given in Appendix I.2; we summarize the results in Table 5.1.

### Table 5.1: Long-wavelength variances and covariances of the elastic properties of soft random solids in the relaxed state.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{kl,p'}$</th>
<th>$\mu_{p'}$</th>
<th>$\lambda_{p'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{ij,p}$</td>
<td>$\theta A_{ijkl}$</td>
<td>$-2\theta p_{ij}^T$</td>
<td>$4\theta p_{ij}^T$</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>$-2\theta p_{kl}^T$</td>
<td>$\nu$</td>
<td>$-2\nu$</td>
</tr>
<tr>
<td>$\lambda_p$</td>
<td>$4\theta p_{kl}^T$</td>
<td>$-2\nu$</td>
<td>$4\nu$</td>
</tr>
</tbody>
</table>

The disorder correlator $[\sigma\sigma]$ features the tensor $A_{ijkl}$, which is defined as

$$A_{ijkl} \equiv 2p_{ij}^T p_{kl}^T + p_{ik}^T p_{jl}^T + p_{il}^T p_{jk}^T,$$

where the projection operator $p^T$ is defined in Section 4.2. The stability condition on the residual stress field $\sigma$ requires that its Fourier transform vanishes when contracted with the momentum $p$. It is straightforward to see that this is obeyed by the disorder correlator $[\sigma\sigma]$ given in Table 5.1, owing to the structure of $A$.

![Figure 5.1: Plot of $Q$, $\theta$ and $\nu$ as functions of the links density parameter $\eta^2$.](image)

The parameters $\theta$ and $\nu$, on which the disorder correlators in Table 5.1
depend, are given by
\begin{align}
\theta & \equiv -\frac{\eta^2 Q^2}{2} + \eta^2 Q - 1 + e^{-\eta^2 Q}, \\
\nu & \equiv -\frac{3}{2} \eta^2 Q^2 + (\eta^2 Q)^2 + \eta^2 Q - 1 + e^\eta^2 Q.
\end{align}

The dependence of $\theta$ and $\nu$ on the density of links $\eta^2$ is shown in Fig. 5.1. The asymptotic behaviors of $\theta$ and $\nu$ are as follows:
\begin{align}
\theta &= \begin{cases} 
\frac{2}{3}(\eta^2 - 1)^3, & \text{for } \eta^2 \gtrsim 1; \\
\eta^2 / 2, & \text{for } \eta^2 \gg 1;
\end{cases} \\
\nu &= \begin{cases} 
\frac{14}{3}(\eta^2 - 1)^3, & \text{for } \eta^2 \gtrsim 1; \\
\eta^4, & \text{for } \eta^2 \gg 1.
\end{cases}
\end{align}

Although the connected disorder correlators of the elastic parameters increase with the density of links $\eta^2$, it is worth noting that the relative fluctuations are decreasing functions of $\eta^2$. For example, the relative fluctuation in shear modulus, defined as $[\mu\mu]_c/[\mu]^2$, scales as
\[ \frac{[\mu\mu]_c}{[\mu]^2} \sim \frac{\nu}{\eta^2}, \]
as shown in Fig. 5.2. This is a decreasing function in the density of links $\eta^2$, which means the relative fluctuations in the shear modulus actually decrease as more links are added. A similar relation for the bulk modulus also holds.

Figure 5.2: Plot of the function $\phi(\eta^2) = \frac{\nu}{\eta^2}$, which characterizes the relative fluctuations in the shear and bulk modulus, and also the connected correlation of the non-affine deformations, as will be shown in Section 5.4.

It is interesting to look at the real-space behavior of disorder correlators of the elastic parameters in the local form of elastic energy. First, it is easy to see that the disorder correlators $[\mu(0)\mu(r)]$, $[\lambda(0)\lambda(r)]$ and $[\mu(0)\lambda(r)]$ are short-ranged in real space: more precisely, they are proportional to $\delta_s(r)$, i.e., to a
Dirac delta-function that has been smoothed on the scale of the short-distance cutoff. This cutoff should be taken to be the typical localization length, in order to validate the Goldstone-fluctuation framework for elastic deformations, because the Goldstone fluctuations in the RLPM are long-wavelength, low-energy excitations of the random solid state, which do not touch lengthscales shorter than the typical localization length.

By contrast, those entities involving the residual stress have a more interesting behavior: in three dimensions and at large lengthscales we have

$$
\begin{align*}
[\sigma_{ij}(0) \sigma_{kl}(\vec{r})]_c &= \frac{(k_B T)^2 n_0 \theta}{\pi |\vec{r}|^4} B_{ijkl}, \\
[\sigma_{ij}(0) \mu(\vec{r})]_c &= -\frac{(k_B T)^2 n_0 \theta}{\pi |\vec{r}|^4} \left(p_{ij}^L(\vec{r}) - p_{ij}^T(\vec{r})\right), \\
[\sigma_{ij}(0) \lambda(\vec{r})]_c &= \frac{2(k_B T)^2 n_0 \theta}{\pi |\vec{r}|^4} \left(p_{ij}^L(\vec{r}) - p_{ij}^T(\vec{r})\right),
\end{align*}
$$

where $p_{ij}^L(\vec{r})$ and $p_{ij}^T(\vec{r})$ are, respectively, longitudinal and transverse projection operators in real space, and are given by

$$
p_{ij}^L(\vec{r}) \equiv \frac{r_i r_j}{|\vec{r}|^2}, \quad p_{ij}^T(\vec{r}) \equiv \delta_{ij} - p_{ij}^L(\vec{r}).
$$

The tensor $B_{ijkl}$ has a complicated structure comprising terms built from projection operators of $\vec{r}$, together with various index combinations, and also depends on the large-momentum cutoff, which can be identified with the inverse of the typical localization length. The dependence on the large-momentum cutoff is a result of keeping only terms of leading order at small momentum $p$ in the calculation of the disorder correlators given in Table 5.1, which enables us to extract the small-momentum behavior in momentum-space, which corresponds to the large-distance behavior in real-space. To Fourier-transform back to real-space, we need a large-momentum cutoff to control the divergence. It turns out that the leading-order behaviors of the real-space disorder correlators $[\sigma \mu]_c$ and $[\sigma \lambda]_c$ at large-distance are independent of this large-momentum cutoff; however, the disorder correlator $[\sigma \sigma]_c$ does depend on it.

### 5.4 Statistics of nonaffine deformations

In this section we calculate the statistics of the nonaffine deformations of the soft random solid state. In Section 4.4 we discussed why soft random solids undergo nonaffine deformations in presence of the given shear deformation $\Lambda$, and explained how to characterize these deformations in terms of the nonaffine deformation field $w_\Lambda$.

The nonaffine deformation field is related to any given nonlocal random kernel $G$ via Eq. (4.24). It is straightforward to see that the disorder average of the nonaffine deformation field vanishes, i.e., $[w_\Lambda] = 0$: it is proportional to the
fluctuation part of the quenched random nonlocal kernel $G^{(1)}$.

Next, we calculate the disorder disorder correlator of the nonaffine deformations. For convenience, we take the incompressible limit, i.e., $\lambda_0 \to \infty$, in which the nonaffine deformation field $w_A$ is given by Eq. (4.27). Using Eq. (4.27) as well as the disorder correlator of the nonlocal kernel $[GG]_c$, the disorder correlator of the nonaffine deformation field $w_A$ is found to be

$$[(w_A)_p \cdot (w_A)_{-p}]_c = \frac{1}{|\rho|^2} n_0 \frac{\nu}{\theta^2} \frac{t_2}{t_1^2} - 1,$$

(5.19)

where

$$t_1 \equiv \text{Tr}(p^T g^{-1}),$$

(5.20a)

$$t_2 \equiv \text{Tr}(p^T g^{-1} g^{-1}),$$

(5.20b)

$$g \equiv \Lambda^T \Lambda.$$  

(5.20c)

The dependence of the connected disorder correlator of the nonaffine deformation field $[w_A w_A]_c$ on the density of links comes through the factor $\phi \equiv \nu/\theta^2$, which is shown in Fig. 5.2. It is evident that, as the density of links increases, the system has smaller relative fluctuations in its elasticity, i.e., the relative fluctuations in the elastic moduli decreases, and thus the nonaffine deformations also decrease, which makes the system less heterogeneous.

The disorder correlator of the nonaffine deformation field, Eq. (5.19), is consistent with the disorder correlator of the nonaffine deformations given in Ref. [70]. In Eq. (3.22) of Ref. [70], the disorder correlator of the nonaffine deformation $u'$ (which corresponds to $v_A$ in our notation) is found to depend on the random local elastic modulus $K_{ijkl}$ in momentum-space as

$$[u'(q) u'(-q)] \propto \frac{\gamma^2 \Delta^K(q)}{q^2 K^2},$$

(5.21)

where $\gamma$ represents the appropriate components of the externally applied deformation (i.e., components of $\Lambda$ in our notation), $\Delta^K$ represents components of the variance of the elastic-modulus tensor, and $K$ represents components of the average of the elastic moduli. The consistency is revealed by taking Eq. (5.19) above, and recalling that $[\mu] \sim \theta$ and $[\mu \mu]_c \sim \nu$, and therefore our disorder correlator of the nonaffine deformation field can be written as

$$[(w_A)_p (w_A)_{-p}]_c \propto \frac{1}{|\rho|^2} \frac{[\mu \mu]_c}{|\mu|^2},$$

(5.22)

which exhibits the same dependence on the mean and variance of the quenched random elastic modulus as Eq. (3.22) of Ref. [70].

Transforming the disorder correlator of the nonaffine deformation field (5.19) back to real space, we found that the large-distance behavior of the disorder correlator of the nonaffine deformation field $[w_A(0) \cdot w_A(r)]_c$ is proportional to

71
in three dimensions, which is also long-ranged.

5.5 Concluding remarks

The heterogeneous elasticity of soft random solids has been investigated via a semi-microscopic approach. By starting with the randomly linked particle model, which is a version of vulcanization theory that studies random networks of particles connected by soft links, we have established a field-theoretic description of the liquid-to-random solid state transition, and analyzed the corresponding pattern of spontaneous symmetry breaking and associated Goldstone fluctuations. We have identified these Goldstone fluctuations as being related to shear deformations of the random solid state and, via this identification, we have obtained a statistical characterization of the quenched randomness exhibited by the heterogeneous elasticity of soft random solids, which features a random nonlocal kernel describing attractive interactions between mass-points.

The heterogeneous elasticity studied via the Goldstone fluctuations in the RLPM is a description of the elastic properties of the state right after linking (i.e., an elastic free energy that takes the state right after linking as its elastic reference state). We have shown that, after linking, the system relaxes to a stable state for any given realization of disorder (i.e., for any given heterogeneous configuration of the elastic parameters in the state right after linking), and this relaxed state, which is a state of mechanical equilibrium, is actually of experiential relevance for soft random solids. By solving for the relaxed state for any given realization of disorder, and expanding the elastic free energy for deformations relative to this relaxed state, we have obtained an elastic free energy relative to the relaxed state (i.e., taking the relaxed state as the new elastic reference state). The statistical description of the quenched randomness in this elastic free energy can then be determined, as we have shown.

The first statistical moments of the quenched random elastic parameters (i.e., the disorder averages of the elastic parameters), unveil the basic homogeneous macroscopic properties of the heterogeneous elastic medium. We have found that the disorder average of the nonlocal kernel of attractive interactions is characterized by the typical localization lengthscale of the RLPM, which is a scale much smaller than the lengthscale of the elastic deformations that we are considering. Thus, it is reasonable to make a local expansion of the elastic energy, relative to the relaxed state. The resulting local form of the elastic energy is a version of Lagrangian elasticity, featuring heterogeneous (i.e., spatially randomly varying) residual stress and Lamé coefficients. The disorder average of the residual stress vanishes. The disorder average of the shear modulus is found to be proportional to temperature, reflecting the entropic nature of the shear rigidity of soft random solids. The disorder average of the bulk modulus depends on the particle number density and the strength of the excluded volume interaction. In particular, the disorder averages of these elastic parameters of
the relaxed state are all translationally and rotationally invariant, reflecting the macroscopic translational and rotational invariances of the soft random solid state.

The second statistical moments of the quenched random elastic parameters (i.e., the spatial correlations of these elastic parameters) characterize the fluctuations of the quenched randomness in the elastic properties. The disorder correlators of the elastic parameters that appear in the local form of the elastic energy relative to the relaxed state exhibit interesting universal behaviors. In particular, the disorder correlators involving the residual stress are found to be long ranged, and governed by a universal parameter that also determines the mean shear modulus, but the disorder correlators of the shear and bulk moduli are short ranged.

Because of the heterogeneity present in the elasticity of soft random solids, upon the application external stress, the system responds by adopting a strain field that is nonaffine (i.e., a strain field that is characterized by an inhomogeneous deformation gradient). We have also obtained a statistical description of these nonaffine deformations. The disorder average of the nonaffine deformations vanishes, and their disorder correlator is also found to be long ranged.

So far, we have studied the first two statistical moments of the quenched random elastic parameters of soft random solids. The whole probability distribution of the quenched random elastic parameters can also be explored using the formalism presented here via the RLPM, and one can also go beyond the local limit of the elasticity theory.

This model of heterogeneous elasticity of soft random solids may also be applied to the study of liquid crystal elastomers, in which the constituent polymers in the random network possesses (or are capable of exhibiting) liquid-crystalline order [71, 72]. In liquid crystal elastomers, the strain field is coupled to the liquid-crystalline order, and this produces a rich collection of interesting phenomena, such as spontaneous sample-shape deformation upon change of temperature, exact soft modes in the elasticity, etc. The interplay of the heterogeneity in the random network and the liquid-crystalline order has interesting consequences: e.g., it can give rise to a polydomain structure in liquid crystal elastomers. The present formalism of heterogeneous elasticity of soft random solids can also provide a framework for the study of the effect of quenched disorder in liquid crystal elastomers [57].
Appendix A

Illustrative examples of the replica trick

In this Appendix, we list two interesting examples to which the replica trick can be applied, confirming results that have been obtained by conventional methods.

The first example is to apply the replica trick on the following integral:

\[ J \equiv - \int_0^\infty e^{-x} \ln x \, dx. \]  \hspace{1cm} (A.1)

This integral gives the Euler–Mascheroni constant \( \gamma \), which is originally defined as

\[ \gamma = \lim_{n \to \infty} \left\{ \sum_{k=1}^n \frac{1}{k} - \ln(n) \right\} \]  \hspace{1cm} (A.2)

and has the numerical value \( \gamma = 0.577216 \ldots \).

We can apply the replica trick

\[ \ln x = \lim_{n \to 0} \frac{x^n - 1}{n}, \]  \hspace{1cm} (A.3)

and define the following sequence of integrals

\[ I(n) = \int_0^\infty e^{-x} x^n \, dx = \Gamma(n + 1). \]  \hspace{1cm} (A.4)

Using this sequence, we have

\[ J = - \lim_{n \to 0} \frac{1}{n} \left( I(n) - I(0) \right) \]
\[ = - \lim_{n \to 0} \frac{1}{n} \left( \Gamma(n + 1) - \Gamma(1) \right) \]
\[ = -\Gamma'(1) \equiv \gamma. \]  \hspace{1cm} (A.5)

So this “difficult” integral \( J \) can be calculated from a limit involving “easy” integrals \( I(n) \).

The second example concerns a thermodynamic system with the following Hamiltonian

\[ H = \frac{1}{2} x^2 + r x \]  \hspace{1cm} (A.6)
where \( x \) is an annealed variable, which thermally fluctuates, and \( r \) is a quenched random variable. For an arbitrarily given \( r \), the partition function is given by

\[
Z(r) = \int_{-\infty}^{\infty} dx \, e^{-\frac{1}{2} x^2 - r x} = \sqrt{2\pi} e^{-\frac{r^2}{2}},
\]

(A.7)

where we have ignored the \( \beta = k_B T \) factor. The free energy for this given \( r \) is then

\[
F(r) = -\ln Z(r) = \frac{1}{2} \ln(2\pi) + \frac{1}{2} r^2.
\]

(A.8)

Choosing the following Gaussian distribution of the quenched random variable \( r \)

\[
P(r) = \frac{1}{\sqrt{2\pi R^2}} e^{-\frac{r^2}{2R^2}},
\]

(A.9)

which gives ([···] denotes disorder average)

\[
[r] = 0, \quad [r^2] = R^2,
\]

(A.10)

we have the disorder averaged free energy

\[
[F] = \frac{1}{2} \ln(2\pi) + \frac{1}{2} R^2.
\]

(A.11)

Can we obtain this result by using replica trick? Using Eq. (1.19), the disorder average of the free energy can be written as

\[
[F] = k_B T \sum_{\chi} P(\chi) \lim_{n \to 0} \frac{Z^n_\chi - 1}{n} = k_B T \lim_{n \to 0} \frac{[Z^n_\chi] - 1}{n}.
\]

(A.12)

In this example the disorder averaged replicated partition function is

\[
[Z(r)^n] = \int dr P(r) \int dx^1 \ldots dx^n \, e^{-\frac{1}{2} \sum_{\alpha=1}^{n} (x^\alpha)^2 - r \sum_{\alpha=1}^{n} x^\alpha}.
\]

(A.13)

We can change the order of the disorder average and the thermal average, perform the disorder average first, and get

\[
[Z(r)^n] = \int dx^1 \ldots dx^n \, e^{-\frac{1}{2} \sum_{\alpha=1}^{n} (x^\alpha)^2 + \frac{R^2}{2} (\sum_{\alpha=1}^{n} x^\alpha)^2}
\]

\[
= \int dx^1 \ldots dx^n \, e^{-\frac{1}{2} x^\alpha M^{\alpha\beta} x^\beta}
\]

(A.14)

where the \( n \times n \) matrix \( M \) is defined as

\[
M^{\alpha\beta} \equiv \delta^{\alpha\beta} - R^2.
\]

(A.15)

Assuming that the eigenvalue spectrum of matrix \( M \) is positive definite, which
is true for integer \( n \), and \( 1 - nR^2 > 0 \), we have

\[
[Z(r)^n] = (2\pi)^{n/2}(\det M)^{-1/2}
\]

(A.16)

It is easy to calculate the eigenvalues of \( M \), so the determinant

\[
\det M = (1 - nR^2) \cdot 1^{n-1}.
\]

(A.17)

Expansion at small \( n \) gives:

\[
\det M \simeq 1 + \frac{n}{2} \ln(2\pi) + \frac{n}{2} R^2 + O(n^2),
\]

(A.18)

so we have the disorder averaged free energy

\[
[F] = k_B T \lim_{n \to 0} \frac{[Z(r)^n] - 1}{n}
\]

\[
= \frac{1}{2} \ln(2\pi) + \frac{1}{2} R^2,
\]

(A.19)

which agrees precisely with the direct computation [Eq. (A.11)]
Appendix B

Disorder averaging with the Deam-Edwards distribution

In this Appendix we calculate the disorder average weighted by the Deam-Edwards distribution, in particular, we calculate $Z_1$ and $Z_{1+n}$ in Section 3.1.

Firstly, we calculate the factor $Z_1$, which is defined as

$$Z_1 \equiv \sum_x \frac{\left( \frac{\eta^2 V_0}{2N\Delta_0^0} \right)^M Z_x (V_0)}{M!}. \quad (B.1)$$

The summation over the quenched disorder $\sum_x$ includes two steps: summation over the number of links $M$, and summation over all possible ways of making these $M$ of links, \textit{i.e.}, assign the $M$ links to different collections of pairs. So Eq. (B.1) can be written as

$$Z_1 = \sum_M \left( \frac{\eta^2 V_0}{2N\Delta_0^0} \right)^M \frac{Z_x (V_0)}{M!} = \sum_{M=0}^{\infty} \sum_{i_1 \neq j_1, i_2 \neq j_2} \cdots \sum_{i_M \neq j_M} \left( \frac{\eta^2 V_0}{2N\Delta_0^0} \right)^M Z_{\mathcal{L}}(V) \left( \prod_{\epsilon=1}^{M} \Delta^{(0)} (|c_{i_\epsilon} - c_{j_\epsilon}|) \right)_{H_0}$$

Mean field approximation on $Z_1$ amounts to taking the number density of the unlinked liquid to be to be $N/V_0$, which is similar to the calculation that yields Eq. (3.15), and we arrive at

$$Z_1 = \exp \left( N \ln V_0 - \frac{N^2 \nu^2}{2V_0 k_B T} \right) \quad (B.3)$$

Secondly, we calculate $Z_{1+n}$, which is defined as

$$Z_{1+n} \equiv \sum_x \frac{\left( \frac{\eta^2 V_0}{2N\Delta_0^0} \right)^M}{M!} Z_x (V_0) Z_x (V)^n. \quad (B.4)$$
The $Z_X(V)^n$ factor can be written in terms of replicas

$$Z_X(V)^n = \int_V \prod_{\alpha=0}^n \prod_{j=1}^N dc_j^\alpha e^{-\sum_{\alpha=0}^n H_0^\alpha/k_BT} \prod_{\alpha=0}^n \prod_{e=1}^M \Delta^{(0)}(|c^\alpha_e - c^\beta_e|), \quad (B.5)$$

where $H_0^\alpha$ is the $H_0$ (i.e., excluded volume interaction) part of the Hamiltonian for the $\alpha$-th replica, as defined in Eq. (3.4).

We define the $H_0$ average for $1+n$ replicas

$$\langle \cdots \rangle_{H_0}^{1+n} = \frac{1}{Z_L(V_0)Z_L(V)^n} \int_{V_0}^N \prod_{i=1}^N dc_i^0 \int_V \prod_{\alpha=1}^n \prod_{i=1}^N dc_i^\alpha e^{-\sum_{\alpha=1}^n H_\alpha/k_BT} \cdots. \quad (B.6)$$

Using this notation we arrive at

$$Z_{1+n} = \sum_{M=0}^\infty \sum_{i_1 \neq j_1}^N \sum_{i_2 \neq j_2}^N \cdots \sum_{i_M \neq j_M}^N \left( \frac{\eta^2 V_0}{2N \Delta^{(0)}} \right)^M \frac{M!}{M!} Z_L(V_0)Z_L(V)^n$$

$$\times \left\langle \prod_{\alpha=0}^n \prod_{e=1}^M \Delta^{(0)}(|c^\alpha_e - c^\beta_e|) \right\rangle_{H_0}^{1+n}$$

$$= Z_L(V_0)Z_L(V)^n \left( \sum_{M=0}^\infty \left( \frac{\eta^2 V_0}{2N \Delta^{(0)}} \right)^M \left( \sum_{i \neq j}^N \prod_{\alpha=0}^n \Delta^{(0)}(|c^\alpha_i - c^\beta_j|) \right) \right)^{H_0}_{1+n}$$

$$= Z_L(V_0)Z_L(V)^n \left( \exp \left( \frac{\eta^2 V_0}{2N \Delta^{(0)}} \sum_{i \neq j}^N \prod_{\alpha=0}^n \Delta^{(0)}(|c^\alpha_i - c^\beta_j|) \right) \right)^{H_0}_{1+n}. \quad (B.7)$$

In this expression the average over the quenched disorder is already performed.
Appendix C

the Hubbard Stratononich Transformation

The effective Hamiltonian [Eq. (3.23)] can be analyzed via the Hubbard-Stratonovich (HS) transformation, which is a powerful method in field theory, and is often applied to strongly constrained models to decouple interactions, yielding standard functional integral representations [73, 74].

The version of HS transformation we used in the RLPM can be illustrated using the following simple example.

Consider a statistical mechanical system with the following partition function

\[ Z = \langle e^{Jq^2 + hq} \rangle_{H_0(q)} = \int dq e^{-H_0(q)} e^{Jq^2 + hq}, \] (C.1)

where \( H(q) = H_0(q) - Jq^2 - hq \) is the total Hamiltonian for the variable \( q \), with \( H_0(q) \) the leading order, and \( Jq^2 \) being considered as a perturbation (although it is just a simple quadratic term here, we use it to illustrate the method). The term \( hq \) denotes the coupling with an external field, which can generate the statistical moments of \( q \) via

\[ \langle q \rangle_{H(q)} = \left. \frac{\partial}{\partial h} \right|_{h=0} \ln Z. \] (C.2)

The \( Jq^2 \) term on exponential can be decoupled using the following version of HS transformation

\[ Z = \left( \frac{J}{\pi} \right)^{1/2} e^{-\frac{h^2}{4J}} \int d\omega e^{-J\omega^2 + h\omega \langle e^{2J\omega q} \rangle_{H_0(q)}} = \left( \frac{J}{\pi} \right)^{1/2} \int d\omega e^{-\mathcal{H}(\omega)}, \] (C.3)

with

\[ \mathcal{H}(\omega) = J\omega^2 - h\omega + \frac{h^2}{4J} - \ln \langle e^{2J\omega q} \rangle_{H_0(q)}. \] (C.4)

In this form, the partition function is expressed as an integral of the variable \( \omega \), and the quadratic term in the original variable \( q \) is already decoupled. If fluctuations with large \( q \) can only appear with very small probabilities, as governed by \( H_0 \), one can expand the \( \ln \langle e^{2J\omega q} \rangle_{H_0(q)} \) term in a series of \( q \), and obtain an effective Hamiltonian \( \mathcal{H}(\omega) \) with leading orders in \( \omega \), which is in a standard
form of Landau free energy, and is convenient to analyze.

It is obvious to see that the average $\omega$ with statistical weight defined by $\mathcal{H}(\omega)$ equals to the average $q$ with statistical weight defined by $H(q)$

$$\langle \omega \rangle_{\mathcal{H}(\omega)} = \left. \frac{\partial}{\partial h} \right|_{h=0} \ln Z = \langle q \rangle_{H(q)}.$$  \hfill (C.5)

Similarly one can prove that higher order statistical moments of $\omega$ and $q$ are also equal via calculating the derivatives with respect to $h$. Thus, the field theory of $q$ can be learned by studying the field theory of $\omega$. In the Hamiltonian $\mathcal{H}(\omega)$, $q$ appears in a linear form, therefore, in cases that $q$ is a variable that involves a summation over many particles, this method allows us to decouple the problem into a single-particle problem, as will be seen in the following application the HS transformation to vulcanization theory.

In RLPM the partition function we are going to decouple is Eq. (3.20)

$$Z_{1+n} = \int \mathcal{D} \Omega \prod_{p \in \mathbb{H}_0} d\Omega_p \prod_{n=1}^{N} \prod_{\alpha=1}^{N} d\omega_{p} e^{-\frac{\mu q_0^2 |q|^2}{k_B T}}, \hfill (C.6)$$

with

$$H_{\Omega}(\Omega_p, \Omega_{\bar{p}}) = \frac{N \eta^2 k_B T}{2 V_n \Delta_0^\alpha} \sum_{\bar{p} \in \mathbb{H}_0} \Omega_{\bar{p}} \Omega_{-\bar{p}} \Delta_{\bar{p}}^{(1+n)} + \frac{\tilde{\nu}^2 N^2}{2 V_0} \sum_p \Omega_{pe}^\alpha \Omega_{-pe}^\alpha$$  \hfill (C.7)

The field $Q_{\bar{p}} = (1/N) \sum_{j=1}^{N} e^{-i \bar{p} \cdot c_j}$ is a complex field, so we need to apply the following equality for complex variables $q$ and $\omega$

$$e^{-J|q|^2} = \frac{J}{\pi} \int d(Re \omega) d(Im \omega) e^{-J|\omega|^2 + 2i J Re q \omega^*}, \hfill (C.8a)$$

$$e^{+J|q|^2} = \frac{J}{\pi} \int d(Re \omega) d(Im \omega) e^{-J|\omega|^2 + 2i J Re q \omega^*}, \hfill (C.8b)$$

notice that the product $Re (q \omega^*) = (Re q)(Re \omega) + (Im q)(Im \omega)$. We use Eq. (C.8a) for the HS transformation for the LRS fields, and Eq. (C.8b) for the HS transformation for the HRS field, and arrive at

$$Z_{1+n} = \int \mathcal{D} \Omega \prod_{n=0}^{N} \mathcal{D} \Omega \prod_{\alpha=0}^{N} e^{-\frac{\mu q_0^2 |q|^2}{k_B T} + \frac{\mu q_0^2 |q|^2}{k_B T} + \frac{\mu q_0^2 |q|^2}{k_B T}}, \hfill (C.9)$$

with

$$H_{\Omega}(\Omega_p, \Omega_{\bar{p}}) = \frac{N \eta^2 k_B T}{2 V_n \Delta_0^\alpha} \sum_{\bar{p} \in \mathbb{H}_0} \Omega_{\bar{p}} \Omega_{-\bar{p}} \Delta_{\bar{p}}^{(1+n)} + \frac{\tilde{\nu}^2 N^2}{2 V_0} \sum_p \Omega_{pe}^\alpha \Omega_{-pe}^\alpha - N k_B T \ln z_0. \hfill (C.10)$$
where the $N k_B T \ln z_0$ is analogous to the $\ln(e^{2J_{eq}})_{H_e(q)}$ term in Eq. (C.4). Using $Q_\hat{P} = (1/N) \sum_{j=1}^N e^{i\hat{p} \hat{c}_j}$, and $Q_\alpha \hat{P} = (1/N) \sum_{j=1}^N e^{i\hat{P}_\alpha \hat{c}_j}$, we have

$$N \ln z_0 \equiv \ln \{ \int \prod_{i=1}^N dc_0^i \int_V \prod_{\alpha=1}^n \prod_{j=1}^N dc_j^\alpha \exp \left[ \frac{N \eta^2}{V N \Delta_{(0)}} \sum_{\hat{p} \in HRS} \Omega_{\hat{p}} \frac{1}{N} \sum_{j=1}^N e^{i\hat{p} \hat{c}_j} \right]$$

$$\times e^{i\hat{p} \hat{c}_j} \Delta_{(1+n)}^{(1+n)} + \frac{i\hat{\nu}^2 N^2}{V k_B T} \sum_{\hat{p}} \Omega_{\hat{p} e^0} \frac{1}{N} \sum_{j=1}^N e^{i\hat{p} \hat{c}_j}$$

$$+ \frac{i\hat{\nu}^2 N^2 V k_B T}{V} \sum_{\alpha=0}^n \sum_{j=1}^N e^{i\hat{p} \hat{c}_j} \}$$

$$= N \ln \left\{ \int dc_0^i \int_V \prod_{\alpha=0}^n dc^\alpha \exp \left[ \frac{\eta^2}{V n \Delta_{(0)}} \sum_{\hat{p} \in HRS} \Omega_{\hat{p}} \Delta_{(1+n)}^{(1+n)} e^{i\hat{p} \hat{c}_j} \right]$$

$$+ \frac{i\hat{\nu}^2 N V k_B T}{V} \sum_{\alpha=0}^n \sum_{j=1}^N e^{i\hat{p} \hat{c}_j} \right\} \right\}. \quad (C.11)$$

In this form it is obvious that the $N$ particles are actually decoupled. Notice that in Eq. (C.9) the functional integrals $\int D\hat{\Omega}_p \prod_{\alpha=0}^n D\hat{\Omega}_p^\alpha$ have carefully chosen prefactors [as in Eq. (C.8)], in order to make the integration properly normalized.
Appendix D

Hamiltonian of the stationary point

In this Appendix we calculate the Hamiltonian of the stationary point, by inserting the stationary point order parameter (3.41) into the Hamiltonian (3.32).

The first term in the Hamiltonian is then

\[
\frac{N\eta^2 k_B T}{2V^n \Delta_0(0)} \sum_{\hat{p} \in HRS} \Omega_{\hat{p}} \Omega_{-\hat{p}} \Delta_{\hat{p}}^{(1+n)}
\]

\[
= \frac{N\eta^2 k_B T}{2V^n \Delta_0(0)} \sum_{\hat{p}} (\Delta(0))^{1+n} e^{-\frac{z^2}{2\bar{\sigma}^2}} \left\{ Q \int \frac{dz_1}{V_0} \int_{\tau_1} e^{-\frac{i\hat{p}^2}{\tau_1^2} - i\hat{p} \hat{z}_c} - Q \delta_{\hat{p}}^{(1+n)d} \right\}
\]

\[
\times \left\{ Q \int \frac{dz_2}{V_0} \int_{\tau_2} e^{-\frac{i\hat{p}^2}{\tau_2^2} + i\hat{p} \hat{z}_c} - Q \delta_{\hat{p}}^{(1+n)d} \right\}
\]

\[
= \frac{N\eta^2 k_B T Q^2}{2V^n \Delta_0(0)} (\Delta(0))^{1+n}
\]

\[
+ \frac{N\eta^2 k_B T Q^2}{2V^n \Delta_0(0)} (\Delta(0))^{1+n} \sum_{\hat{p}} \int \frac{dz_1 dz_2}{V_0^2} \int_{\tau_1, \tau_2} e^{\left( \frac{1}{\tau_1^2} + \frac{1}{\tau_2^2} + \frac{a^2}{2}\right) |\hat{p}|^2 - i\hat{p} (\hat{z}_c, 1 - \hat{z}_c, 2)}
\]

\[
= \frac{N\eta^2 k_B T Q^2 (\Delta(0))^n}{2V^n}
\]

\[
+ \frac{N\eta^2 k_B T Q^2 (\Delta(0))^n}{2V^n} \left( 1 + n \zeta^2 \right)^{d/2} \int_{\tau_1, \tau_2} \left\{ 2\pi \left( \frac{1}{2\tau_1} + \frac{1}{2\tau_2} + \frac{a^2}{2}\right) \right\}^{-nd/2},
\]

(D.1)

where \( \hat{z}_c \equiv \{ z, \zeta z, \ldots, \zeta^d \} \). The sum \( \sum_{\hat{p} \in HRS} \) is changed into \( \sum_{\hat{p}} \) because the order parameter we inserted-in has a vanishing LRS. We have also changed momentum summation into an integral via \( \frac{1}{V^n} \sum_{\hat{p}} = \int \frac{d^{(1+n)d}}{(2\pi)^{1+n} \bar{\sigma}^d} \).

The free energy of the system is related to the \( O(n) \) term of this Hamiltonian, as given by Eq. (3.11,3.12). Thus, we can make the small \( n \) expansion. It is straightforward to see that \( O(1) \) terms cancel, and the leading order is \( O(n) \)

\[
\frac{N\eta^2 k_B T}{2V^n \Delta_0(0)} \sum_{\hat{p} \in HRS} \Omega_{\hat{p}} \Omega_{-\hat{p}} \Delta_{\hat{p}}^{(1+n)}
\]

\[
= n \frac{N\eta^2 k_B T Q^2}{2V^n} \left\{ \ln V - \frac{d}{2} \left( \ln(2\pi) + \zeta^2 \right) - \frac{d}{2} \int_{\tau_1, \tau_2} \left( \frac{1}{2\tau_1} + \frac{1}{2\tau_2} + \frac{a^2}{2}\right) \right\}. \quad (D.2)
\]

Similarly one can also calculate the \( \ln z_0 \) term. Insert the saddle point order
parameter into $z_0$, and sum (integrate) over momentum $\hat{p}$ we have

$$
z_0 = \int d\hat{p} \int_{V_0}^n d\alpha \exp \left\{ \frac{\eta^2}{V} \sum_{\rho \in HRS} \Omega_\rho \Delta_\rho^{(1+n)} e^{i\hat{p} \cdot \hat{z}} \right\}
= e^{-\eta^2 Q(\Delta_0^{(0)}/V)^n} \int d\hat{c} \exp \left\{ \eta^2 Q(\Delta_0^{(0)})^n \int dz \int_\tau \left( \frac{\tilde{\tau}}{2\pi} \right)^{\frac{(1+n)d}{2}} e^{-\frac{\tilde{\tau}^2}{2(\tau_1 + \cdots + \tau_m)}} \right\},
$$

(D.3)

where $\tilde{\tau} \equiv \left( \frac{1}{\tau} + a^2 \right)^{-1}$. Then we can write the exponential in its Taylor expansion (keeping to all orders) and integrate out $\hat{c}$

$\newpage$

$$
z_0 = e^{-\eta^2 Q(\Delta_0^{(0)}/V)^n} V_0 V^n \left\{ 1 + \eta^2 Q(\Delta_0^{(0)}/V)^n \right\}
+ \frac{1}{V_0 V^n} \sum_{m=2}^{\infty} \frac{(\eta^2 Q(\Delta_0^{(0)})^n)^m}{m!} \int dz_1 \cdots dz_m
\times \int_{\tau_1, \ldots, \tau_m} m \prod_{j=1}^{\tau_j} \left( \frac{2\pi}{\tau_1 + \cdots + \tau_m} \right)^{\frac{(1+m)\tau_j}{2}} e^{-\frac{\tau_j^2}{2(\tau_1 + \cdots + \tau_m)}} \right\},
$$

(D.4)

where on the exponential, the terms following $(\tilde{z}_\xi - \tilde{z}_\zeta, \tilde{z})^2$ includes all pairs between the $m$ variables [there are $m(m - 1)/2$ terms]. Using $(\tilde{z}_\xi - \tilde{z}_\zeta, \tilde{z})^2 = (1 + n\zeta^2)(z_1 - z)^2$ (recall that $\tilde{z}_\xi$ is a $(1+n)$d-dimensional vector, and $z_1$ is a d-dimensional vector), the integration $\int dz_1 \cdots dz_m$ can be easily performed, and we have

$$
z_0 = e^{-\eta^2 Q(\Delta_0^{(0)}/V)^n} V_0 V^n \left\{ 1 + \eta^2 Q(\Delta_0^{(0)}/V)^n \right\}
+ \frac{1}{V_0 V^n} \sum_{m=2}^{\infty} \frac{(\eta^2 Q(\Delta_0^{(0)})^n)^m}{m!} \int dz_1 \cdots dz_m
\times \int_{\tau_1, \ldots, \tau_m} m \prod_{j=1}^{\tau_j} \left( \frac{2\pi}{\tau_1 + \cdots + \tau_m} \right)^{\frac{(1+m)\tau_j}{2}} (1 + n\zeta^2)^{\frac{(1-m)d}{2}} \right\}.
$$

(D.5)

Then $-\ln z_0$ is obtained by make small $n$ expansion, using the following equality

$$
\ln(x + ny + O(n^2)) = \ln(x(1 + n(y/x) + O(n^2))) = \ln x + n(y/x) + O(n^2),
$$

(D.6)

so we have

$$
-\ln z_0 = -\ln V_0 + n \left\{ -\ln V + (\eta^2 Q + e^{-\eta^2 Q} - 1) \left\{ \frac{d}{2} (\ln(2\pi) + \zeta^2) - \ln V \right\}
- e^{-\eta^2 Q} \frac{d}{2} \sum_{m=1}^{\infty} \frac{(\eta^2 Q)^m}{m!} \ln \left( \frac{\tau_1 \cdots \tau_m}{\tau_1 + \cdots + \tau_m} \right) \right\}.
$$

(D.7)

Therefore the small $n$ expansion of the stationary point Hamiltonian $H^{(SP)}_{\Omega}$
to $O(n)$ is given by

$$
H^{(SP)}_\Omega = \frac{\tilde{h}_0^2(0) N^2}{2V_0} + \frac{n\tilde{h}_0^2(0) N^2}{2V} - Nk_BT \ln V_0 - nNk_BT \ln V
$$

$$
+ nNk_BT \left\{ \theta \left( \frac{d}{2} \left( \ln(2\pi) + \zeta^2 \right) - \ln V \right)
- \frac{\eta^2 Q^2}{2} \frac{d}{2} \int_{\tau_1, \tau_2} \ln \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2 \right)
- e^{-\eta^2 Q} \sum_{n=1}^{\infty} \frac{(\eta^2 Q)^m}{m!} \int_{\tau_1, \ldots, \tau_2} \ln \left( \frac{\tilde{\tau}_1 \cdots \tilde{\tau}_m}{\tau_1 + \cdots + \tau_m} \right) \right\}, \quad (D.8)
$$

where the parameter

$$
\theta \equiv -\frac{\eta^2 Q^2}{2} + \eta^2 Q + e^{-\eta^2 Q} - 1. \quad (D.9)
$$
Appendix E

Hamiltonian of the Goldstone-deformed state

In this Appendix we calculate the Hamiltonian of the Goldstone deformed order parameter, by inserting the Goldstone deformed order parameter (3.60) into the Hamiltonian (3.32), following a similar calculation in Appendix D. To yield a description of elasticity, we shall expand the Hamiltonian for small deformations, in particular, in a series of the small scalar variable characterizing the replicated deformation field $\Psi_R(z_1, z_2) \equiv (\tilde{R}(z_1) - \tilde{R}(z_2))^2 - (1 + n)(z_1 - z_2)^2$.

The quadratic term in the Hamiltonian is

$$\frac{N\eta^2 k_B T}{2Vn} \sum_{\rho \in HRS} \Omega_\rho \Delta_\rho^{(1+n)}$$

$$= \frac{N\eta^2 k_B T}{2Vn} \sum_{\rho} (\Delta^{(0)})^{1+n} e^{-\frac{|\beta|^2}{2}} \left\{ Q \int \frac{dz_1}{V_0} \int_{\tau_1} e^{-\frac{|\beta|^2}{2} - i\beta \cdot \tilde{R}(z_1)} - Q\delta_\rho^{(1+n)d} \right\}$$

$$\times \left\{ Q \int \frac{dz_2}{V_0} \int_{\tau_2} e^{-\frac{|\beta|^2}{2} + i\beta \cdot \tilde{R}(z_2)} - Q\delta_\rho^{(1+n)d} \right\}$$

$$= \frac{N\eta^2 k_B T Q^2 (\Delta^{(0)})^n}{2Vn} + \frac{N\eta^2 k_B T Q^2 (\Delta^{(0)})^n}{2Vn} Vn \int \frac{dz_1 dz_2}{V_0^2} \int_{\tau_1, \tau_2} \left[ 2\left( \frac{1}{2\tau_1} + \frac{1}{2\tau_2} + \frac{\alpha^2}{2} \right) \right]^{-\frac{(1+n)d}{2}} e^{-\frac{1}{2} \left( \frac{\tilde{R}(z_1) - \tilde{R}(z_2))^2}{2} \right)}.$$

Now we can expand in small $\Psi_R$ using the notation $\Psi_R(z_1, z_2) \equiv (\tilde{R}(z_1) - \tilde{R}(z_2))^2 - (1 + n)(z_1 - z_2)^2$. Note that $\Psi_R$ is not related to the deformation relative to the stationary point, which is characterized by the mean positions of the replicas of the particle $\hat{z}_\zeta = \{z, \zeta z, \ldots, \zeta z\}$, instead, it describes deformations relative to the “state right after linking” (i.e., prior to relaxation), characterized by the mean positions of the replicas of the particle $\hat{z} = \{z, \ldots, z\}$, as discussed in Section 3.4.3 and 4.2. The expansion of the quadratic term is given.
by

\[
\frac{N\eta^2 k_BT}{2V^n} \Delta_0^{(0)} \sum_{\rho \in HRS} \Omega_{\rho} \Omega_{-\rho} \Delta_{\rho}^{(1+n)}
\]

\[
= \frac{N\eta^2 k_BTQ^2}{2V^n} (\Delta_0^{(0)})^n + \frac{N\eta^2 k_BTQ^2}{2} (\Delta_0^{(0)})^n \int \frac{dz_1 dz_2}{V_0} \int_{\tau_1, \tau_2}
\]

\times \left[ 2\pi \left( \frac{1}{2\tau_1} + \frac{1}{2\tau_2} + \frac{a^2}{2} \right) \right] \left( \frac{\Psi_R(z_1, z_2)}{2\left( \frac{1}{2\tau_1} + \frac{1}{2\tau_2} + \frac{a^2}{2} \right)} \right)^2 \times \left\{ 1 \right\}

The small \( n \) expansion on this quadratic term is given by:

\[
\frac{N\eta^2 k_BT}{2V^n} \Delta_0^{(0)} \sum_{\rho \in HRS} \Omega_{\rho} \Omega_{-\rho} \Delta_{\rho}^{(1+n)}
\]

\[
= n \frac{N\eta^2 k_BTQ^2}{2} \left\{ \ln V - \frac{d}{2} (\ln(2\pi) + 1) - \frac{d}{2} \int_{\tau_1, \tau_2} \ln \left( \frac{1}{2\tau_1} + \frac{1}{2\tau_2} + \frac{a^2}{2} \right) \right\}
\]

\[
+ \int \frac{dz_1 dz_2}{V_0} \int_{\tau_1, \tau_2} \left\{ 2\pi \left( \frac{1}{2\tau_1} + \frac{1}{2\tau_2} + \frac{a^2}{2} \right) \right\} \left( \frac{\Psi_R(z_1, z_2)}{2\left( \frac{1}{2\tau_1} + \frac{1}{2\tau_2} + \frac{a^2}{2} \right)} \right)^2 \times \left\{ 1 \right\}
\]

\[
+ O(n^2)
\]

The calculation for the \( \ln z_0 \) term is similar to the above calculation for the quadratic term. the expansion in small variable \( \Psi_R \) reads

\[
z_0 = e^{-\eta^2 Q(\Delta_0^{(0)}/V)^n} V_0 V^n \left\{ 1 + \eta^2 Q(\Delta_0^{(0)}/V)^n
\]

\[
+ \frac{1}{V_0 V^n} \sum_{m=2}^{\infty} \frac{(\eta^2 Q(\Delta_0^{(0)})^n)^m}{m!} \int \frac{dz_1 \cdots dz_m}{\tau_1, \cdots, \tau_m}
\]

\[
\times \prod_{j=1}^{m} \left( \frac{2\pi}{2\tau_i} \right)^{\frac{1+n+m}{2}} \left( \frac{2\pi}{\tau_i + \tau_m} \right)^{\frac{1+n+m}{2}} e^{-\frac{1}{2\tau_i} \frac{(z_1 + \cdots + z_m)^2}{\tau_i + \tau_m}}
\]

\[
\times \left\{ 1 \right\}
\]

\[
+ O(n^2)
\]

\[
\text{(E.4)}
\]

where the summations that we have abbreviated into \( \cdots \) includes all pairs formed by \( \{z_1, \ldots, z_m\} \). We then expand in small \( n \) and keep to \( O(n) \) in the \( \ln z_0 \) term, assuming that \( \Psi_R(z_1, z_2) \) is of \( O(n) \), because it contains a summation

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\[ \sum_{\alpha=1}^n. \] After a tedious calculation we have

\[
\begin{align*}
-\ln z_0 &= -\eta^2 Q \left( \frac{\Delta^{(0)}}{V} \right)^n - \ln V_0 - n \ln V - \eta^2 Q \\
&\quad - ne^{-\eta^2 Q} \left\{ (1 - e^{\eta^2 Q}) \ln V + \eta^2 Q e^{\eta^2 Q} \ln V_0 \\
&\quad + (e^{\eta^2 Q} - 1 - \eta^2 Q e^{\eta^2 Q}) \frac{d}{2} (\ln (2\pi) + 1) \\
&\quad + \frac{d}{2} \sum_{m=1}^{\infty} \int_{\tau_1, \ldots, \tau_m} \ln \left( \frac{\hat{\tau}_1 \cdots \hat{\tau}_m}{\tau_1 + \cdots + \tau_m} \right) \\
&\quad - e^{-\eta^2 Q} \frac{1}{V_0} \sum_{m=2}^{\infty} \frac{(\eta^2 Q)^m}{m!} \int dz_1 \cdots dz_m \int_{\tau_1, \ldots, \tau_m} \prod_{j=1}^{m} \left( \frac{\hat{\tau}_j}{2\pi} \right)^{\frac{d}{2}} \left( \frac{2\pi}{\hat{\tau}_1 + \cdots + \hat{\tau}_m} \right)^{\frac{d}{2}} \\
&\quad \times e^{-\frac{\eta^2 Q}{2(\hat{\tau}_1 + \cdots + \hat{\tau}_m)} \left( \hat{\tau}_1 \hat{\tau}_2 \Psi_R(z_1, z_2) + \cdots \right)} \\
&\quad + \frac{1}{2} \left( \frac{\hat{\tau}_1 \hat{\tau}_2 \Psi_R(z_1, z_2) + \cdots}{2(\hat{\tau}_1 + \cdots + \hat{\tau}_m)} \right)^2 + O(\Psi_R^3).
\end{align*}
\]

(E.5)

In order to further simplify the expression, first consider the \( O(\Psi_R) \) terms in the expansion, \( \hat{\tau}_1 \hat{\tau}_2 \Psi_R(z_1, z_2) + \cdots \). The first term has a factor \( \Psi_R(z_1, z_2) \equiv (R(z_1) - R(z_2))^2 - (1 + n)(z_1 - z_2)^2 \) which only involves two variables \( z_1 \) and \( z_2 \), so we can integrate out the other \( (m - 2) \) variables, \( z_3, \ldots, z_m \). (Of course, for \( m = 2 \), no integrals are needed.) In total, there are \( \frac{m(m - 1)}{2} \) (number of pairs among \( m \) variables) such terms. Thus, the \( O(\Psi_R) \) terms in \( -\ln z_0 \) is given by

\[
\begin{align*}
&\quad - e^{-\eta^2 Q} \frac{1}{V_0} \sum_{m=2}^{\infty} \frac{(\eta^2 Q)^m}{m!} \int dz_1 \cdots dz_m \int_{\tau_1, \ldots, \tau_m} \prod_{j=1}^{m} \left( \frac{\hat{\tau}_j}{2\pi} \right)^{\frac{d}{2}} \left( \frac{2\pi}{\hat{\tau}_1 + \cdots + \hat{\tau}_m} \right)^{\frac{d}{2}} \\
&\quad \times e^{-\frac{\eta^2 Q}{2(\hat{\tau}_1 + \cdots + \hat{\tau}_m)} \left( \hat{\tau}_1 \hat{\tau}_2 \Psi_R(z_1, z_2) + \cdots \right)} \\
&\quad + \frac{1}{2} \left( \frac{\hat{\tau}_1 \hat{\tau}_2 \Psi_R(z_1, z_2) + \cdots}{2(\hat{\tau}_1 + \cdots + \hat{\tau}_m)} \right)^2 + O(\Psi_R^3).
\end{align*}
\]

(E.6)

where in the last line here we used the fact that \( \{ z_1, z_2, \ldots, z_m \} \) are symmetric, so the \( \frac{m(m - 1)}{2} \) terms are identical.

Similarly for the \( O(\Psi_R^3) \) terms in the expansion in Eq. (E.5), there are terms involving two points such as \( \Psi_R(z_1, z_2)^2 \), three points such as \( \Psi_R(z_1, z_2) \Psi_R(z_1, z_3) \), and four points such as \( \Psi_R(z_1, z_2) \Psi_R(z_3, z_4) \) (Of course, for \( m = 3 \) there is no four point terms, and for \( m = 2 \) there is no three or four points terms.) Thus
the $O(\Psi_R^2)$ terms can be written as

$$\left[\tilde{\tau}_1 \tilde{\tau}_2 \Psi_R(z_1, z_2) + \cdots\right]^2$$

$$- \frac{1}{4(\tilde{\tau}_1 + \cdots + \tilde{\tau}_m)^2} \left[\frac{m(m-1)}{2} \tilde{\tau}_1^2 \tilde{\tau}_2^2 \Psi_R(z_1, z_2)^2 + m(m-1)(m-2) \tilde{\tau}_1^2 \tilde{\tau}_3 \Psi_R(z_1, z_2) \Psi_R(z_2, z_3) + \frac{m(m-1)(m-2)(m-3)}{4} \tilde{\tau}_1 \tilde{\tau}_2 \tilde{\tau}_3 \tilde{\tau}_4 \Psi_R(z_1, z_2) \Psi_R(z_3, z_4)\right]. \quad (E.7)$$

Following a similar calculation as in Eq. (E.6), we can integrate out the integration variables that are not present in $\Psi_R$, and obtain the $O(\Psi_R^2)$ term in ln $z_0$.

Summing up the contributions from the quadratic term and the ln $z_0$ term, we arrive at the Hamiltonian of the Goldstone deformed state

$$H_{\Omega}^{(GS)} = H_{\Omega}^{(SP)} + H_{\Omega}^{\Psi_R}, \quad (E.8)$$

with $H_{\Omega}^{(SP)}$ being the Hamiltonian of the stationary point, and the increase of the Hamiltonian due to Goldstone deformation is given by

$$H_{\Omega}^{\Psi_R} = -Nk_B T \frac{\theta d}{2} \zeta^2 + \frac{1}{2} \int dz_1 dz_2 K_1(z_1, z_2) \Psi_R(z_1, z_2) - \frac{1}{8k_B T} \int dz_1 dz_2 dz_3 dz_4 K_2(z_1, z_2, z_3, z_4) \Psi_R(z_1, z_2) \Psi_R(z_3, z_4). \quad (E.9)$$

The first term here, $-Nk_B T \frac{\theta d}{2} \zeta^2$, is present due to the fact that the expansion variable $\Psi_R(z_1, z_2)$ is from the state right after linking, not the stationary point, as we have previously discussed. Note that $H_{\Omega}^{\Psi_R}$ only involves the energy of shear deformation, because the Goldstone modes only contains pure shear deformations, and the energy of volume variations is in the stationary point Hamiltonian part, which has a variable contraction parameter $\zeta$. The kernels in Eq. (E.9) are given by

$$\frac{1}{2} K_1(z_1, z_2)$$

$$= \frac{N \eta^2 k_B T Q^2}{4V_0} \int_{\tilde{\tau}_1, \tilde{\tau}_2} \left(2\pi \left(\frac{1}{\tilde{\tau}_1} + \frac{1}{\tilde{\tau}_2} + \alpha^2\right)\right)^{-d/2} \frac{\Gamma\left(\frac{1}{\tilde{\tau}_1} + \frac{1}{\tilde{\tau}_2} + \alpha^2\right)}{\Gamma\left(\frac{1}{\tilde{\tau}_1} + \frac{1}{\tilde{\tau}_2}\right)} e^{-\frac{(\tilde{\tau}_1 - \tilde{\tau}_2)^2}{\left(\frac{1}{\tilde{\tau}_1} + \frac{1}{\tilde{\tau}_2}\right)}}$$

$$+ \frac{Nk_B T}{2V_0} e^{-\eta^2 \tilde{Q}} \sum_{m=2}^{\infty} \frac{(\eta^2 Q)^m}{m!} \frac{m(m-1)}{2} \int_{\tilde{\tau}_1, \ldots, \tilde{\tau}_m} \left(\frac{\tilde{\tau}_1 \tilde{\tau}_2}{2\pi(\tilde{\tau}_1 + \tilde{\tau}_2)}\right)^{d/2}$$

$$\times e^{-\frac{\tilde{\tau}_1 \tilde{\tau}_2(z_1 - z_2)^2}{2(\tilde{\tau}_1 + \tilde{\tau}_2)^2}} \frac{\tilde{\tau}_1 \tilde{\tau}_2}{\tilde{\tau}_1 + \cdots + \tilde{\tau}_m} \quad (E.10)$$
and

\[
-\frac{1}{8k_BT} K_2(z_1, z_2, z_3, z_4) = \frac{N\eta^2 k_BTQ^2}{16V_0} \int_{\tilde{T}_1, \tilde{T}_2} \left(2\pi \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2\right)\right)^{-d/2} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2\right)^{-1}
\]

\[
\times e^{-z\left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2\right)} \delta(d)(z_1 - z_3)\delta(d)(z_2 - z_4)
\]

\[
-\frac{Nk_BT}{8V_0} e^{-\eta^2 Q} \sum_{m=2}^{\infty} \frac{(\eta^2 Q)^m}{m!} \int_{\tilde{T}_1, \ldots, \tilde{T}_m} \left(\frac{\tilde{T}_1\tilde{T}_2}{2\pi(\tilde{T}_1 + \tilde{T}_2)}\right)^{d/2}
\]

\[
\times e^{-\frac{\tau_1\tau_2(z_1-z_2)^2 + \tau_3\tau_4(z_3-z_4)^2 + \tau_5\tau_6(z_5-z_6)^2}{2(\tilde{T}_1 + \tilde{T}_2 + \tilde{T}_3 + \tilde{T}_4 + \tilde{T}_5 + \tilde{T}_6)}} \delta(d)(z_1 - z_3)\delta(d)(z_2 - z_4)
\]

\[
-\frac{Nk_BT}{8V_0} e^{-\eta^2 Q} \sum_{m=3}^{\infty} \frac{(\eta^2 Q)^m}{m!} \frac{1}{m-2}(m-3) \int_{\tilde{T}_1, \ldots, \tilde{T}_m} \left(\frac{\tilde{T}_1\tilde{T}_2\tilde{T}_3}{4\pi^2(\tilde{T}_1 + \tilde{T}_2 + \tilde{T}_3)}\right)^{d/2}
\]

\[
\times e^{-\frac{\tau_1\tau_2(z_1-z_2)^2 + \tau_3\tau_4(z_3-z_4)^2 + \tau_5\tau_6(z_5-z_6)^2}{2(\tilde{T}_1 + \tilde{T}_2 + \tilde{T}_3 + \tilde{T}_4 + \tilde{T}_5 + \tilde{T}_6)}} \delta(d)(z_1 - z_3)\delta(d)(z_2 - z_4)
\].

(E.11)

Strictly speaking, the kernel \(K_2\) should be symmetric under the exchange of the variables \(z_1 \leftrightarrow z_2\) or \(z_3 \leftrightarrow z_4\). Here to save space we used the above non-symmetric form. The true symmetric form can be recovered by

\[
K_2(z_1, z_2, z_3, z_4) \rightarrow \frac{1}{4} \left(K_2(z_1, z_2, z_3, z_4) + K_2(z_1, z_2, z_4, z_3) + K_2(z_2, z_1, z_3, z_4) + K_2(z_2, z_1, z_4, z_3)\right).
\]

(E.12)
Appendix F

Relaxation of the phenomenological elastic energy

In this Appendix we solve the stationarity condition for the random local deformations $v$. Firstly we need to calculate the variation of the “bulk term”, which can be expanded to leading order in small $v$ as

\[
\det \left( \frac{\partial R_i(z)}{\partial z_j} \right) = \det \left( \zeta \delta_{ij} + \partial_j v_i(z) \right) \\
\approx \zeta^d \left( 1 + \zeta^{-1} \partial_i v_i(z) \right). \quad (F.1)
\]

Using this we have

\[
\left\{ \det \left( \frac{\partial R_i(z)}{\partial z_j} \right) - 1 \right\}^2 = \left( \zeta^d - 1 \right)^2 + 2(\zeta^d - 1)\zeta^{d-1} \partial_i v_i(z) \\
+ \zeta^{2d-2} \partial_i v_i(z) \partial_j v_j(z). \quad (F.2)
\]

Thus, the stationarity equation is

\[
0 = 2(\zeta z_a + v_a(z)) \int dz_2 G(z, z_2) \\
- 2 \int dz_2 G(z, z_2)(\zeta z_{2,a} + v_a(z_2)) - \lambda'_0 \partial_a (\partial_i v_i(z)), \quad (F.3)
\]

where

\[
\lambda'_0 \equiv \lambda_0 \zeta^{2d-2}. \quad (F.4)
\]

We take the disorder average of the nonlocal kernel, $G^{(0)}$, to be zeroth order, and the fluctuation part, $G^{(1)}$, to be first order, thus $v(z)$ is also first order. So the zeroth order equation is

\[
0 = 2z_a \int dz_2 G^{(0)}(z - z_2) - 2 \int dz_2 G^{(0)}(z - z_2) z_{2,a}, \quad (F.5)
\]

which is automatically satisfied given that $G^{(0)}(z - z_2)$ is even in $(z - z_2)$.

\[1\] A similar expansion but to higher order in $v$ is performed in Eq. (G.11), in terms of the strain tensor $\epsilon$. 

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The first order equation is

\[ 0 = \zeta z_a \int dz_2 G^{(0)}(z, z_2) + v_a(z) \int dz_2 G^{(0)}(z - z_2) - \int dz_2 G^{(1)}(z, z_2) z_{2,a} - \int dz_2 G^{(0)}(z - z_2) v_a(z) - \frac{\lambda_0'}{2} \partial_z (\partial_z v_i(z)). \] (F.6)

This equation can be solved in momentum space. We define the following Fourier transforms (on a finite volume which is the volume of the state right after linking \( V_0 \))

\[ G_p^{(0)} = \int dx e^{-ipx} G^{(0)}(x), \]

\[ G_{p_1,p_2}^{(1)} = \int dx e^{-ip_{1}x_1 - ip_{2}x_2} G^{(0)}(x_1, x_2), \] (F.7)

so the momentum space stationarity equation is

\[ 0 = i\zeta \frac{\partial}{\partial p_{1,a}} G_{p_1,p_2}^{(1)} \bigg|_{p_2=0} - i\zeta \frac{\partial}{\partial p_{2,a}} G_{p_1,p_2}^{(1)} + (G_p^{(0)} - G_{p_1}^{(0)}) v_{a,p_1} + \frac{\lambda_0'}{2} \delta_{i,a} \delta_{a,b} v_{b,p_1}. \] (F.8)

Strictly speaking, the differentiation here should be understood as difference quotient instead because we are using a finite volume version of the Fourier transform, but for convenience we just write it as differentiation.

This equation can be written in the tensorial form

\[ \left\{ 2 \left( \frac{D_p}{p^2} \right) P^T + \left( \lambda_0' \frac{D_p}{p^2} + \frac{D_p}{p^2} \right) L \right\} \cdot |p|^2 \vec{v}_p = \vec{f}_p, \] (F.9)

where

\[ f_{a,p} \equiv -2\zeta \left( i \frac{\partial}{\partial p_{a}} G_{p_0,p_0}^{(1)} - i \frac{\partial}{\partial p_{2,a}} G_{p_1,p_2}^{(1)} \right), \] (F.10)

which is actually the random force in the state that is contracted but not yet equilibrated for randomness, and

\[ D_p \equiv G_p^{(0)} - G_p^{(0)}. \] (F.11)

\( I \) is the \( d \)-dimensional identity matrix, and the projection operators in momentum space are defined as

\[ p_{ij}^L \equiv p_i p_j / p^2, \]

\[ p_{ij}^T \equiv \delta_{ij} - p_i p_j / p^2, \] (F.12)
which satisfy the following relations

\[(p^L)^2 = p^L, \quad (p^T)^2 = p^T, \quad p^L \cdot p^T = 0.\] (F.13)

In the following we use bold letters to denote rank-2 tensors, and letters with an overhead arrow (such as \(\vec{v}(p)\)) to denote a vector when needed.

By this decomposition we arrive at the solution to Eq. (F.9)

\[
\vec{v}_p = \frac{p^T \cdot \vec{f}_p}{2D_p} + \frac{p^L \cdot \vec{f}_p}{\lambda_0 |p|^2 + 2D_p}. \] (F.14)

Notice that the second term is much smaller than the first term, due to the large bulk modulus \(\lambda_0\). In the incompressible limit \(\lambda_0 \to \infty\), we have

\[
\vec{v}_p = \frac{p^T \cdot \vec{f}_p}{2D_p}, \] (F.15)

which is a purely transverse field, meaning that it satisfies \(p_i v_{i,p} = 0\) or \(\partial_i v_i(x) = 0\), which is the only deformation allowed in an incompressible media.
Appendix G

Re-expanding the elastic energy around the equilibrium reference state

In this Appendix we re-expand the elastic energy for deformations relative to the relaxed state \( \tilde{z} = \zeta z + v(z) \), as discussed in Section 4.3. The small variable in this expansion is the deformation field \( \tilde{u}(\tilde{z}) \) relative to the relaxed state. Furthermore, to obtain a continuous description of the elasticity, we shall adopt the notation with the strain tensor

\[
\epsilon_{ij}(x) \equiv \frac{1}{2} (\Lambda_{ij}(x) - \delta_{ij}) = \frac{1}{2} (\partial_i u_j(x) + \partial_j u_i(x) + \partial_i u_l(x) \partial_j u_l(x)).
\]

(G.1)

where \( \Lambda_{ij}(x) \equiv \partial R_i(x) / \partial x_j \) is the deformation gradient tensor. This strain tensor transform as a tensor in the reference space labeled by \( x \), and as a scalar in the target space labeled by \( R \).

G.1 Expanding the nonlocal kernel \( \tilde{G} \)

in the relaxed state The definition of \( \tilde{G} \), as given in Section 4.3, is

\[
\tilde{G}(\tilde{z}_1, \tilde{z}_2) \equiv G(z(\tilde{z}_1), z(\tilde{z}_2)).
\]

(G.2)

It can be expanded in small \( v \) to yield a direct expression for \( \tilde{G} \). In momentum-space

\[
\tilde{G}_{p_1, p_2} = \int dz_1 dz_2 e^{-i p_1 \tilde{z}_1 - i p_2 \tilde{z}_2} \tilde{G}(\tilde{z}_1, \tilde{z}_2) = \int dz_1 dz_2 e^{-i p_1 z_1 - i p_2 z_2} G(z(z_1), z(z_2))
\]

\[
= \int dz_1 dz_2 \mathcal{J}(z_1) \mathcal{J}(z_2) e^{-i p_1 (\zeta z_1 + v(z_1)) - i p_2 (\zeta z_2 + v(z_2))} G(z_1, z_2),
\]

(G.3)

where in the first line \( z(\tilde{z}_1) \) is the mapping of a mass point \( \tilde{z}_1 \) in the relaxed state back to the position \( z(\tilde{z}_1) \) where it was in the state right after linking. Plugging in the expression for \( \zeta \) and \( v(z) \), given by Eq. (4.5, 4.9), and keep to \( O((1/\lambda_0)^0) \), which gives \( \zeta \simeq 1 \) and \( \mathcal{J}(z) \simeq 1 \), we can expand \( v \) down, and keep
to first order in $G^{(1)}$ ($v$ is in the same order as $G^{(1)}$), and arrive at

\[
\tilde{G}_{\tilde{p}_1, \tilde{p}_2} \
\simeq \int dz_1 dz_2 (1 - i\tilde{p}_1 v(z_1) - i\tilde{p}_2 v(z_2)) e^{-i\tilde{p}_1 \cdot z_1 - i\tilde{p}_2 \cdot z_2 (G^{(0)}(z_1, z_2) + G^{(1)}(z_1, z_2))} 
\]

\[
\simeq G^{(0)}_{\tilde{p}_1, \tilde{p}_2} + G^{(1)}_{\tilde{p}_1, \tilde{p}_2} - i \int dz_1 dz_2 (\tilde{p}_1 v(z_1) + \tilde{p}_2 v(z_2)) e^{-i\tilde{p}_1 \cdot z_1 - i\tilde{p}_2 \cdot z_2 G^{(0)}(z_1, z_2)} 
\]

\[
= G^{(0)}_{\tilde{p}_1, \tilde{p}_2} + G^{(1)}_{\tilde{p}_1, \tilde{p}_2} - i (\tilde{p}_1 \cdot v(\tilde{p}_1 + \tilde{p}_2) G^{(0)}_{\tilde{p}_2} + \tilde{p}_2 \cdot v(\tilde{p}_1 + \tilde{p}_2) G^{(0)}_{\tilde{p}_1}). \tag{G.4}
\]

### G.2 Local expansion of the harmonic attraction

In this section we make a local expansion of the nonlocal term in the elastic energy of the equilibrium reference state

\[
\Gamma_{\text{nonlocal}} = \frac{1}{2} \int d\tilde{z} d\tilde{z} \mathcal{J}(z_1)^{-1} \mathcal{J}(z_2)^{-1} \tilde{G}(\tilde{z}_1, \tilde{z}_2) \times \left( |\tilde{R}(\tilde{z}_1) - \tilde{R}(\tilde{z}_2)|^2 - |\tilde{z}_1 - \tilde{z}_2|^2 \right). \tag{G.5}
\]

For convenience of notation, we define the following change of variables

\[
z = z_1,
\]

\[
y = z_2 - z_1,
\]

\[
M(z, y) \equiv \tilde{G}(z_1, z_2), \tag{G.6}
\]

so that the nonlocal kernel in relaxed state, Eq. (4.16), can be written as (in momentum space)

\[
\tilde{M}_{\tilde{p}, \tilde{q}} \simeq M^{(0)}_{\tilde{p}, \tilde{q}} + M^{(1)}_{\tilde{p}, \tilde{q}} + g_{\tilde{p}, \tilde{q}} (f_{\tilde{p}} \cdot \mathbf{p}^T \cdot \tilde{q}) \tag{G.7}
\]

with the definition and leading order in momentum expansion of $g_{\tilde{p}, \tilde{q}}$ given by

\[
g_{\tilde{p}, \tilde{q}} \equiv \frac{i (G^{(0)}_{\tilde{q}} - G^{(0)}_{\tilde{p}, \tilde{q}})}{2(G^{(0)}_{\tilde{p}} - G^{(0)}_{\tilde{q}})} \simeq \frac{i (\tilde{p}^2 - 2\tilde{p} \cdot \tilde{q})}{2\tilde{p}^2}. \tag{G.8}
\]

The local expansion of Eq. (G.5) is then given by

\[
\Gamma_{\text{nonlocal}} = \frac{1}{2} \int d\tilde{z} d\tilde{y} \tilde{M}(\tilde{z}, \tilde{y}) \left( |\tilde{R}(\tilde{z}) - \tilde{R}(\tilde{z} + \tilde{y})|^2 - |\tilde{y}|^2 \right) 
\]

\[
\simeq \frac{1}{2} \int d\tilde{z} (\partial_j \tilde{R}_j(\tilde{z}) - \partial_i \tilde{R}_i(\tilde{z}) - \delta_{ij}) \int d\tilde{y} \tilde{y}_i \tilde{y}_j \tilde{M}(\tilde{z}, \tilde{y}), \tag{G.9}
\]

where the factor $\mathcal{J}(z_1)^{-1} \mathcal{J}(z_2)^{-1}$ is ignored because its difference from unity is of $O(1/\lambda_0)$. Using the strain tensor $\hat{e}_{ij}(\tilde{z}) = \frac{1}{2} (\partial_i \tilde{R}_j(\tilde{z}) - \partial_j \tilde{R}_i(\tilde{z}) - \delta_{ij})$, it is straightforward to express this term in a local form, which is the standard form of Lagrangian elasticity.

The complete expression of the local form of elastic energy for deformations
relative to the relaxed state, including the contribution from the bulk term, will be calculated in Appendix G.4.

G.3 Expansion of the “bulk term”

The “bulk term” in the elastic free energy Eq. (4.14) is

$$\Gamma_{\text{bulk}} \equiv \frac{\lambda_0}{2} \int d\tilde{z} J(z)^{-1} \left\{ J(z) \det \left( \frac{\partial \tilde{R}_i(\tilde{z})}{\partial \tilde{z}_j} \right) - 1 \right\}^2.$$  \hspace{1cm} \text{(G.10)}

The determinant can be expanded using the strain tensor $\tilde{\epsilon}$

$$\det \left( \frac{\partial \tilde{R}_i(\tilde{z})}{\partial \tilde{z}_j} \right) = \det(\tilde{\Lambda}(\tilde{z})) = \det(I + 2\tilde{\epsilon}(\tilde{z}))^{1/2} = e^{\frac{1}{2} \text{Tr} \ln(I + 2\tilde{\epsilon}(\tilde{z}))}.$$  \hspace{1cm} \text{(G.11)}

Thus we have

$$\Gamma_{\text{bulk}} = \frac{\lambda_0}{2} \int d\tilde{z} J(z)^{-1} \left\{ J(z) \det \left( \frac{\partial \tilde{R}_i(\tilde{z})}{\partial \tilde{z}_j} \right) - 1 \right\}^2$$

$$\simeq \frac{\lambda_0}{2} \int d\tilde{z} J(z)^{-1} \left\{ (J(z) - 1)^2 + 2(J(z) - 1)J(z)\text{Tr}\tilde{\epsilon}(\tilde{z}) \right.$$

$$\left. - 2(J(z) - 1)J(z)(\text{Tr}\tilde{\epsilon}(\tilde{z}))^2 + (2J(z) - 1)J(z)(\text{Tr}\tilde{\epsilon}(\tilde{z}))^2 \right\}.$$  \hspace{1cm} \text{(G.12)}

Inserting the solutions of $\zeta$ and $v$, as given in Eq. (4.5, 4.9), into the Jacobian $J(z) \equiv |\frac{\partial \tilde{z}}{\partial z}|$, we arrive at

$$\Gamma_{\text{bulk}} = \int d\tilde{z} \left\{ \text{Tr}(\sigma'(\tilde{z}) \cdot \tilde{\epsilon}(\tilde{z})) + \mu(\tilde{z})\text{Tr}\tilde{\epsilon}(\tilde{z})^2 + \frac{\lambda(\tilde{z})}{2}(\text{Tr}\tilde{\epsilon}(\tilde{z}))^2 \right\}.$$  \hspace{1cm} \text{(G.13)}

with the elastic parameters (in momentum space)

$$\sigma'_{ij,p} = \delta_{ij} \left\{ \frac{ip \cdot \tilde{f}_\rho}{p^2} - \rho V_0 \delta_\rho \right\}$$

$$\mu_\rho = \rho V_0 \delta_\rho - \frac{ip \cdot \tilde{f}_\rho}{p^2}$$

$$\lambda_\rho = \lambda_0 V_0 \delta_\rho + 2 \left\{ \frac{ip \cdot \tilde{f}_\rho}{p^2} - \rho V_0 \delta_\rho \right\}.$$  \hspace{1cm} \text{(G.14)}

G.4 Local form of the elastic energy relative to the relaxed state

Summing up the contributions from the nonlocal term $\Gamma_{\text{nonlocal}}$ and the bulk term $\Gamma_{\text{bulk}}$ in the elastic free energy (4.14), we arrive at the local form of the
elastic energy for deformations relative to the relaxed state

\[ \Gamma = \int d\tilde{z} \left\{ \text{Tr}(\sigma(\tilde{z}) \cdot \mathbf{\dot{e}}(\tilde{z})) + \mu(\tilde{z})\text{Tr}(\mathbf{\dot{e}}(\tilde{z}))^2 + \frac{\lambda(\tilde{z})}{2}(\text{Tr}(\mathbf{\dot{e}}(\tilde{z}))^2) \right\}, \]  

\[ \text{(G.15)} \]

with the elastic parameters

\[ \sigma_{ij, \tilde{p}} = -\frac{\partial^2}{\partial \tilde{q}_i \partial \tilde{q}_j} \mid_{\tilde{q}_0} \sigma^{(1)}_{\tilde{p}, \tilde{q}_\tilde{p}} + i\delta_{ij} \frac{i\tilde{p} \cdot \mathbf{\dot{f}}_\tilde{p}}{|\tilde{p}|^2} - \frac{f_{a, \tilde{p}}}{|\tilde{p}|^2} (\tilde{p}_i \tilde{p}_j + \tilde{p}_j \tilde{p}_i), \]  

\[ \mu_{\tilde{p}} = \rho V_0 \delta_{\tilde{p}} - \frac{i\tilde{p} \cdot \mathbf{\dot{f}}_\tilde{p}}{|\tilde{p}|^2} \]  

\[ \lambda_{\tilde{p}} = \lambda_0 V_0 \delta_{\tilde{p}} + 2 \left\{ \frac{i\tilde{p} \cdot \mathbf{\dot{f}}_\tilde{p}}{|\tilde{p}|^2} - \rho V_0 \delta_{\tilde{p}} \right\}. \]  

\[ \text{(G.16a)} \]

\[ \text{(G.16b)} \]

\[ \text{(G.16c)} \]
Appendix H

Relaxation of the deformed state and nonaffine deformations

In this section we solve for the stationarity equation with a given macroscopic deformation \( \Lambda \), as discussed in Section 4.4, which yield information about non-affine deformations. The stationarity condition is given by

\[
2(\zeta_{\Lambda ai} z_i + (v_\Lambda)_a(z)) \int dz_2 G(z, z_2) - 2 \int dz_2 G(z, z_2)(\zeta_{\Lambda ai} z_{2i} + (v_\Lambda)_a(z_2)) - \lambda'_0 \Lambda^{-1}_{ia} \Lambda^{-1}_{jb} \partial_i \partial_j (v_\Lambda)_b(z) = 0. \tag{H.1}
\]

We take \( G^{(0)} \) to be zeroth order, and \( G^{(1)} \) and \( v_\Lambda(z) \) to be first order. So the zeroth order equation is

\[
0 = 2\Lambda_{ai} z_i \int dz_2 G^{(0)}(z - z_2) - 2\Lambda_{ai} \int dz_2 G^{(0)}(z - z_2)z_{2i} \tag{H.2}
\]

which is already satisfied given that \( G^{(0)}(z - z_2) \) is even in \( (z - z_2) \).

The first order equation is

\[
\zeta_{\Lambda ai} z_i \int dz_2 G^{(1)}(z, z_2) + (v_\Lambda)_a(z) \int dz_2 G^{(0)}(z, z_2) - \int dz_2 G^{(0)}(z, z_2)(v_\Lambda)_a(z_2) - \frac{\lambda'_0}{2} \Lambda^{-1}_{ia} \Lambda^{-1}_{jb} \partial_i \partial_j (v_\Lambda)_b(z) = 0. \tag{H.3}
\]

We can also solve it in momentum-space, in which the equation is expressed as

\[
0 = i\zeta_{\Lambda ai} \partial_{p_{1i}} G^{(1)}_{p_1,0} - i\zeta_{\Lambda ai} \partial_{p_{2i}} \bigg|_{p_{2i}=0} G^{(1)}_{p_1,p_2} + (G^{(0)}_0 - G^{(0)}_p)(v_\Lambda)_a_{p_1} + \frac{\lambda'_0}{2} \Lambda^{-1}_{ia} \Lambda^{-1}_{jb} p_{1i} p_{1j} (v_\Lambda)_b_{p_1} \tag{H.4}
\]

This equation can be written in the tensorial form

\[
\left\{ \frac{2D_p}{|p|^2} I + \lambda'_0 \Lambda^{-T} \Lambda^{-1} \right\} \cdot |p|^2 (v_\Lambda)_p = (f_\Lambda)_p, \tag{H.5}
\]

where \( g = \Lambda^T \Lambda \) is the metric tensor, and

\[
D_p \equiv G^{(0)}_0 - G^{(0)}_p, \tag{H.6a}
\]

\[
(f_\Lambda)_{a,p} \equiv -2\zeta \left( i\Lambda_{ai} \partial_{p_{1i}} G^{(1)}_{p_1,0} - i\Lambda_{ai} \partial_{p_{2i}} \bigg|_{p_{2i}=0} G^{(1)}_{p_1,p_2} \right). \tag{H.6b}
\]
To solve the equation we define the deformed version of the projection operators

\[
\begin{align*}
\mathbf{p}_L^\Lambda & \equiv \frac{1}{\text{Tr}(\mathbf{p}^L \mathbf{g}^{-1})} \Lambda^{-T} \mathbf{p}^L \Lambda^{-1}, \\
\mathbf{p}_T^\Lambda & \equiv \mathbf{I} - \mathbf{p}_L^\Lambda.
\end{align*}
\]

(H.7a) (H.7b)

It is easy to verify that

\[
\begin{align*}
(\mathbf{p}_L^\Lambda)^2 &= \mathbf{p}_L^\Lambda, \\
(\mathbf{p}_T^\Lambda)^2 &= \mathbf{p}_T^\Lambda, \\
\mathbf{p}_L^\Lambda \cdot \mathbf{p}_T^\Lambda &= 0.
\end{align*}
\]

(H.8)

Using these deformed projection operators we can write Eq. (H.5) as

\[
\begin{align*}
\left\{ \frac{2D_p}{|p|^2} \mathbf{p}_T^\Lambda + \left( \frac{2D_p}{|p|^2} + \lambda_0 t_1 \right) \mathbf{p}_L^\Lambda \right\} \cdot |p|^2 (v_\Lambda)_p = (\mathbf{f}_\Lambda)_p,
\end{align*}
\]

where we have defined

\[
t_1 \equiv \text{Tr}(\mathbf{p}^T \mathbf{g}^{-1}).
\]

(H.9) (H.10)

It is straightforward to arrive at the solution

\[
\begin{align*}
(v_\Lambda)_p &= \left\{ \frac{\mathbf{p}_T^\Lambda}{2D_p} + \frac{\mathbf{p}_L^\Lambda}{\lambda_0 t_1 |p|^2 + 2D_p} \right\} \cdot (\mathbf{f}_\Lambda)_p.
\end{align*}
\]

(H.11)
Appendix I

Disorder correlators of elastic parameters in the relaxed state

I.1 Disorder correlator of the nonlocal kernel in the relaxed state

The nonlocal kernel $\tilde{G}$ in the relaxed state is related to the nonlocal kernel $G$ in the state right after linking via Eq. (4.15a), and in leading order in small $v$, as in Eq. (4.16), we have

$$
\tilde{G}_{\tilde{p}_1, \tilde{p}_2} \simeq G_{\tilde{p}_1, \tilde{p}_2}^{(0)} + G_{\tilde{p}_1, \tilde{p}_2}^{(1)} - i\left(\tilde{p}_1 \cdot \tilde{v}_{(\tilde{p}_1 + \tilde{p}_2)\tilde{p}_2} G_{\tilde{p}_1, \tilde{p}_2}^{(0)} + \tilde{p}_2 \cdot \tilde{v}_{(\tilde{p}_1 + \tilde{p}_2)\tilde{p}_1} G_{\tilde{p}_1, \tilde{p}_2}^{(0)}\right). \quad (I.1)
$$
Using this relation, we can derive the correlation function of \( \tilde{G} \) from the correlation function of \( G \), which is given in Eq. (5.7b), and we arrive at

\[
[M_{p_1, q_1} \cdot \mathcal{M}_{p_2, q_2}]^c = \delta_{p_1+p_2} \left\{ - \frac{N \eta^2 Q^2}{2k_B T} \int_{\tau_1, \tau_2} \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2 \right)^{-2} \times \left( e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1 + q_2|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 - q_1 + q_2|^2} \right) / 2 \\
+ \frac{N}{(k_B T)^2} e^{-\eta^2 Q} \sum_{m=2}^{\infty} \frac{(\eta^2 Q)^m}{m!} \int_{\tau_1, \ldots, \tau_m} \left( \frac{\tau_1 \tau_2}{\tau_1 + \cdots + \tau_m} \right)^2 \times \left( e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1 + q_2|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 - q_1 + q_2|^2} \right) / 2 \\
+ m(m-1)(m-2) \int_{\tau_1, \ldots, \tau_m} \left( \frac{\tau_1 \tau_2}{\tau_1 + \cdots + \tau_m} \right)^2 \times \left( e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1 + q_2|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 - q_1 + q_2|^2} \right) / 4 \\
+ m(m-1)(m-2)(m-3) \int_{\tau_1, \ldots, \tau_m} \left( \frac{\tau_1 \tau_2}{\tau_1 + \cdots + \tau_m} \right)^2 \times \left( e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1 + q_2|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 - q_1 + q_2|^2} \right) \right\} \\
+ 2i \delta_{p_1+p_2} q_1 \cdot \mathbf{p}_1^\top \mathbf{q}_2 \left\{ - \frac{N \eta^2 Q^2}{2k_B T} \int_{\tau_1, \tau_2} \left( \frac{1}{\tau_1} + \frac{1}{\tau_2} + a^2 \right)^{-1} \times \left[ t_{p_1, q_1} (e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 + q_1|^2} / 2 \right] \\
- t_{-p_1, q_2} (e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 - q_1|^2} / 2) \right\} \\
+ \frac{N}{(k_B T)^2} e^{-\eta^2 Q} \sum_{m=2}^{\infty} \frac{(\eta^2 Q)^m}{m!} \int_{\tau_1, \ldots, \tau_m} \left( \frac{\tau_1 \tau_2}{\tau_1 + \cdots + \tau_m} \right)^2 \times \left( t_{p_1, q_1} (e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 + q_1|^2}) / 2 \right) \\
- t_{-p_1, q_2} (e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 - q_1|^2}) / 2 \right) \\
+ m(m-1)(m-2) \int_{\tau_1, \ldots, \tau_m} \left( \frac{\tau_1 \tau_2}{\tau_1 + \cdots + \tau_m} \right)^2 \times \left( t_{p_1, q_1} (e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 + q_1|^2}) / 4 \right) \\
- t_{-p_1, q_2} (e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |q_1|^2} + e^{-\frac{1}{2} \left( \frac{p_1^2}{\tau_1} + \frac{p_2^2}{\tau_2} + a^2 \right) |p_1 - q_1|^2}) / 4 \right) \right\},
\]

where we have used the notation \( M(z, y) \equiv \tilde{G}(z_1, z_2) \) defined in Appendix (G.2).
I.2 Disorder correlators of the elastic parameters in the local form

In this appendix we calculate the disorder correlators of the quenched random elastic parameters in the local form of the elastic energy of deformations relative to the relaxed state.

Firstly we calculate the disorder correlator of the residual stress \([\sigma_{ij} c]_{ij} c\). The residual stress \(\sigma\) in the relaxed state is related to the nonlocal kernel \(G\) via Eq. (4.19a). Thus the correlator of the residual stress can be expressed as

\[
[\sigma_{ij} c]_{ij} c = \frac{\partial}{\partial q_{ij}} \bigg|_{q_1=0,q_2=0} [N_{j,p_1,q_1} N_{i,p_2,q_2}] c \\
- \frac{2}{|p_1|^2} \left( p_{1,b} P_{bl}^T(p_1) + p_{1,a} P_{al}^T(p_1) \right) \frac{\partial}{\partial q_{1,i}} \bigg|_{q_1=0} [N_{j,p_1,q_1} N_{i,p_2,q_2}] c \\
+ \frac{2}{|p_1|^2} \left( p_{1,a} P_{aj}^T(p_1) + p_{1,b} P_{bj}^T(p_1) \right) \frac{\partial}{\partial q_{2,k}} \bigg|_{q_2=0} [N_{j,p_1,q_1} N_{i,p_2,q_2}] c \\
- \frac{2}{|p_1|^2} \left( p_{1,a} P_{aj}^T(p_1) + p_{1,b} P_{bj}^T(p_1) \right) \left( p_{1,a} P_{aj}^T(p_1) + p_{1,b} P_{bj}^T(p_1) \right) \left( N_{j,p_1,a} N_{i,p_2,b} \right) c
\]

where we have defined \(N_{j,p_1,q_1} \equiv \frac{\partial M_{j,p_1}}{\partial q_{1,i}}\), and the notation \(M(z,y) \equiv G(z_1,z_2)\) is defined in Appendix (G.2).

Then we can plug in the disorder correlator \([M_{p_1,q_1} M_{p_2,q_2}] c\), given in Eq. (5.7b) (in the form of \([GG]\)). After a tedious calculation, and using the following identity

\[
m \int_{\tau_1,\ldots,\tau_m} \frac{\tilde{\tau}_2^2}{(\tilde{\tau}_1 + \cdots + \tilde{\tau}_m)^2} + m(m-1) \int_{\tau_1,\ldots,\tau_m} \frac{\tilde{\tau}_1 \tilde{\tau}_2}{(\tilde{\tau}_1 + \cdots + \tilde{\tau}_m)^2} = 1,
\]

we arrive at

\[
[\sigma_{ij} c]_{ij} c = \delta_{p_1+p_2} \frac{N\theta}{(k_B T)^2} (2 \mu_{ij}^T P_{bl}^T + \mu_{ij}^T P_{aj}^T + \mu_{ij}^T P_{bj}^T).
\]

where \(\theta \equiv -\frac{\eta^2 Q}{2} + \eta^2 Q - 1\) is given in Eq. (D.9).

Following a similar calculation, we also calculated the disorder correlators and cross-correlators of the quenched random elastic parameters in the local form of elasticity of the relaxed state. We arrive at the correlators of the shear modulus and the bulk modulus

\[
[\mu_{p_1} \mu_{p_2}] c = \nu \delta_{p_1+p_2} N(k_B T)^2,
\]

\[
[\lambda_{p_1} \lambda_{p_2}] c = 4\nu \delta_{p_1+p_2} N(k_B T)^2,
\]
where the dimensionless parameter

\[ \nu \equiv \frac{3}{2} \eta^2 Q^2 + \nu Q - 1 + \eta^2 Q + (\eta^2 Q)^2. \]  

(I.7)

The cross-correlators are given by

\[
[\sigma_{ij,p_1\mu} p_2]_c = -2N(k_B T)^2 \theta \delta_{p_1+p_2} \mathbf{p}_{ij}^T(p_1), \tag{I.8a}
\]

\[
[\sigma_{ij,p_1\lambda} p_2]_c = 4N(k_B T)^2 \theta \delta_{p_1+p_2} \mathbf{p}_{ij}^T(p_1), \tag{I.8b}
\]

\[
[\mu_{p_1\lambda} p_2]_c = -2N(k_B T)^2 \nu \delta_{p_1+p_2}, \tag{I.8c}
\]

where \( \theta \) is defined in Eq. (D.9), and \( \nu \) is defined in Eq. (I.7).
References


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Xiaoming Mao was born on Feb 6, 1980, in Xi’an, a beautiful historical city in China. She received her Bachelor of Science in Physics in 2002, with a minor in Economics, from Peking University in Beijing, China. She received her Master of Science in Physics in 2004 from University of Illinois at Urbana-Champaign.