Elasticity of highly cross-linked random networks

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Abstract. – Starting from a microscopic model of randomly cross-linked particles with quenched disorder, we calculate the Landau-Wilson free energy $S$ for arbitrary cross-link densities. Considering pure shear deformations, $S$ takes the form of the elastic energy of an isotropic amorphous solid state, from which the shear modulus can be identified. It is found to be a universal quantity, not depending on any microscopic length-scales of the model.

Introduction. – It is well known that randomly cross-linked networks of molecules undergo a transition from a fluid to an amorphous solid state, as the number of cross-links is increased. This sol-gel transition has been studied in detail [1–4] in recent years, and the structure as well as the elasticity [5,6] is well understood. However, almost all theoretical studies have focussed on the near-critical region, where the analysis simplifies due to the existence of a small parameter — the distance to the critical point or, equivalently, the order parameter. In contrast, the highly cross-linked regime has hardly been investigated [7], yet it is particularly interesting in the application of random network models to glasses [8].

In this paper we consider a particularly simple network which is built from spherical particles, connected by harmonic springs. This allows us to access the highly cross-linked regime and compute the shear modulus for arbitrary cross-link concentration. We find that the shear modulus is independent of all microscopic length scales of the model, such as the spring constant and the length scale that characterizes the localisation of particles in the amorphous solid state. Instead, the shear modulus is completely determined by the density of cross-links or, equivalently, the gel fraction.

Model: randomly cross-linked particles. – We consider a system of $N$ identical particles at positions $\{R_1, \ldots, R_N\}$ in a $d$-dimensional volume $V$. Permanent cross-links connect $M$ randomly chosen particles, such that a particular cross-link realization $C$ is specified by a list of $M$ pairs of monomers $C = \{(i_1, j_1), \ldots, (i_M, j_M)\}$. The cross-links are modelled by harmonic springs:

$$H_{\text{Xlink}} = \frac{1}{2a^2} \sum_{e=1}^{M} (R_{i_e} - R_{j_e})^2.$$  

(1)
Here, the parameter \(a\) can be interpreted as the typical length of a cross-link. (Energies are measured in units of \(k_B T\).) Furthermore, a repulsive excluded-volume interaction \(H_{ev}\) is introduced to prevent the system from collapsing. The overall Hamiltonian is \(H = H_{\text{Xlink}} + H_{ev}\). All thermodynamic properties, including the elastic ones, can be obtained from the partition function \(Z(C) = \int d^\beta \mathcal{R}_1 \cdots d^\beta \mathcal{R}_N e^{-H}\), which depends on the quenched disorder \(C\) that specifies the configuration of cross-links.

The average over all cross-link configurations \(C\) is called the \textit{disorder average} and denoted by \([\cdot]\). A realistic choice of the cross-link distribution is the Dean-Edwards distribution [1]:

\[
P_{DE}(C) \propto \frac{1}{M!} \left( \frac{V}{2N} \frac{\mu^2}{a^d(2\pi)^{d/2}} \right)^M Z(C).
\]

(2)

Its parameter \(\mu^2\) determines the probability for a cross-link to be formed, and therefore controls the sol-gel transition. The average cross-link density is given by \([M]/N = \mu^2/2\) and the standard deviation, relative to the mean, vanishes in the thermodynamic limit. Thus, \(\mu^2 = 2[M]/N\) is the \text{average coordination number}, \text{i.e.}, the average number of particles to which a certain particle is connected. For a detailed discussion of the Dean-Edwards distribution, see [3,7].

\textbf{Order parameter and free energy. –} With help of the replica technique we obtain the disorder-averaged free energy \(F = -[\ln Z] = -\lim_{m \to 0} (\bar{Z}_{n+1} - \bar{Z}_1)/(n \bar{Z}_1)\). The replica partition function \(\bar{Z}_{n+1} = \int \mathcal{D} \Omega e^{-S_\Omega}\) is represented as a functional integral over the order-parameter field, whose expectation value

\[
\bar{\Omega}(\hat{x}) = \frac{1}{N} \sum_{i=1}^{N} \left( \delta(x^{(0)} - R^{(0)}_i) \cdots \delta(x^{(n)} - R^{(n)}_i) \right)_{S_\Omega}
\]

(3)

quantifies the probability of finding a particle at position \(x^{(0)}\) in replica 0, at \(x^{(1)}\) in replica 1, etc. Here, the average \((\cdot)_{S_\Omega}\) is evaluated with the statistical weight \(e^{-S_\Omega}\). To simplify the notation, we have introduced \(d(n+1)\)-dimensional hatted vectors \(\hat{x} = (x^{(0)}, \ldots, x^{(n)})\). Previous work [9] has shown that the saddle-point solution for the order parameter has the following simple form: A fraction of monomers \((1 - Q)\) is delocalized and can be found anywhere in the sample with equal probability. The remaining fraction \(Q\) is the “infinite” cluster and each particle \(i\) performs Gaussian fluctuations —in each replica— about a mean position \(y_i\) with localization length \(\xi_i\). The mean positions \(y_i\) are randomly distributed and the localization lengths \(\xi\) follow the distribution \(P(\xi^2)\). The resulting order parameter is explicitly given by

\[
\bar{\Omega}(\hat{x}) = \frac{1 - Q}{V_n} + \frac{Q}{V} \int d^d y \int_0^\infty \frac{d\xi^2}{(2\pi \xi^2)^{d(n+1)/2}} P(\xi^2) \exp \left(-\sum_{\alpha=0}^{n} \frac{(x_\alpha - y_\alpha)^2}{2\xi^2} \right),
\]

(4)

with self-consistent equations for \(Q\) and \(P(\xi^2)\) given in [7,9]. Note that the order parameter does not depend on \(\sum_{\alpha=0}^{n} x_\alpha\).

The Landau-Wilson free energy

\[
S_\Omega = \frac{\mu^2}{2} \sum_{\hat{k}} \Delta(\hat{k}) \left| \Omega(\hat{k}) \right|^2 - \ln \left( \int \frac{d^{d(n+1)} R}{V_n} \exp \left( \mu^2 \sum_{\hat{k}} \Delta(\hat{k}) \Omega(\hat{k}) e^{-i\hat{k} R} \right) \right)
\]

(5)

is particularly simple, because we consider cross-linked particles instead of cross-linked chains. This will allow us to perform computations in the \textit{highly cross-linked limit}. The function \(\Delta(\hat{k}) = \exp(-\frac{1}{2} \frac{a^2 \hat{k}^2}{2})\) reflects the harmonic potential for the cross-links (1), and \(\hat{k} := (k^{(0)}, \ldots, k^{(n)})\). The symbol \(\sum_{\hat{k}}\) means summation over all \(\hat{k}\’s\) with at least two non-zero components \(k^{(\alpha)}\).
Spontaneously broken translational invariance. – The effective replicated Hamiltonian is invariant under uniform translations of all particles, separately in each replica, i.e., \( R^\alpha_i \rightarrow R^\alpha_i + u^\alpha \) is an exact symmetry of the Hamiltonian\(^{(1)}\). In the amorphous solid phase, which is characterized by random localisation of a finite fraction of particles, this symmetry is spontaneously broken, and the only symmetries remaining are common displacements of all replicas, i.e., \( R^\alpha_i \rightarrow R^\alpha_i + u \), reflecting the macroscopic translational invariance of the amorphous solid phase. (For a detailed discussion see [5,6].) Consequently, there is a whole family of order parameters that each give rise to the same free energy and are related by replica-dependent, spatially uniform translations. To distinguish common and relative displacements of the replicas, it is helpful to split up the \( (n+1)\)-dimensional hatted vectors \( \hat{x} \) into \( d\)-dimensional longitudinal ones \( x^\parallel = 1/\sqrt{n+1}(x^{(1)},\ldots,x^{(n)}) \) and \( dn\)-dimensional transverse ones \( x^\perp = \hat{x} - 1/\sqrt{n+1}(x^\parallel,\ldots,x^\parallel) \). The manifold of symmetry-related saddle points is parameterized by \( u^\perp = \hat{u} - 1/\sqrt{n+1}(u^\parallel,\ldots,u^\parallel) \):

\[
\Omega_{u^\perp}(\hat{x}) = 1 - Q/V^{n+1} + \frac{Q}{V(n+1)d^2} \int_0^\infty \frac{d\xi^2 P(\xi^2)}{(2\pi\xi^2)^{dn+1}} \exp \left( -\frac{(x^\perp - \hat{u})^2}{2\xi^2} \right).
\]

The situation is illustrated in fig. 1a, where the order parameter is shown for two replicas in one space-dimension. The order parameter does not depend on \( x^\parallel \), so that it is represented by a rectilinear ridge having its maximum height along the axis \( x^\perp = 0 \) and having width \( \xi \). The family of symmetry-related solutions is generated by rigidly translating the ridge to a new position: \( x^\perp = u^\perp \). (The delocalized particles contribute only an unimportant constant background \( (1-Q)/V^{n+1} \), which has been ignored in the figure.)

\(^{(1)}\)The effective replicated Hamiltonian is also invariant under uniform rotations, separately in each replica. However, the spontaneous breaking of this symmetry does not give rise to Goldstone modes and is not discussed further.
Goldstone fluctuations. – Low-energy excitations are constructed by particle displacements \(u_\perp(x_\parallel)\) that depend on the position in the sample \([5,6]\). The ridge is not translated rigidly, but deformed by the position-dependent vector \(u_\perp(x_\parallel)\), as indicated in fig. 1b. These excitations do cost energy; only in the long-wavelength limit do we expect the energy of excitation to vanish with an inverse power of the wavelength. The generalized order parameter fluctuations take the form \([10]\)

\[
\Omega_{u_\perp}(\hat{x}) = \frac{1 - Q}{V(n+1)} + \frac{Q}{V(n+1)^{d/2}} \int_0^\infty \frac{d\xi^2 P(\xi^2)}{(2\pi \xi^2)^{d(n+1)/2}} \int d^d y_\parallel e^{-\frac{|y_\parallel^2 + (x_\parallel - u_\perp(y_\parallel))^2}{2\xi^2}}. \tag{7}
\]

We only consider pure shear deformations, and hence require that \(|\det(\partial_{\nu} + \partial_{\nu} u_{\alpha}^\perp})| = 1\). This constraint is consistent with taking the excluded-volume interaction to be large, which makes the system incompressible. For small deformations, the constraint simplifies to \(\partial_{\nu} u_{\alpha}^\perp = 0\).

We insert the Ansatz (7) into the general expression (5) for the free energy and only consider small distortions, so that it is sufficient to keep \(u_\perp\) only to the lowest order, \((\partial u_\perp/\partial x_\parallel)^2\). Higher orders in \(u_\perp\) and higher-order derivatives are neglected. Restoring units of energy, the resulting free energy is

\[
S_{u_\perp} = S_{u_\perp=0} + \frac{G}{2} \lim_{n \to 0} \frac{1}{n} \int q^d x_\parallel \sum_\alpha \sum_{\nu,\mu} \left(\frac{\partial u_\perp^{(\alpha)}(y_\parallel)}{\partial x_\parallel^{(\mu)}}\right)^2, \tag{8a}
\]

with the shear modulus \(G\) given by

\[
G = \left(\mu^2 Q - 1 + \exp(-\mu^2 Q) - \frac{\mu^2 Q^2}{2}\right) n_0 k_B T, \tag{8b}
\]

where \(n_0 = N/V\) is the mean particle density.

The part of the Landau-Wilson free energy (8a) that does not depend on \(u_\perp\) determines the gel fraction and the distribution of localization lengths that was discussed in \([7]\). In particular, differentiating \(S_{u_\perp=0}\) with respect to \(Q\) yields a simple relation between the gel fraction \(Q\) and the average coordination number \(\mu^2\): \(\exp(-\mu^2 Q) = 1 - Q\), which is shown in fig. 2. It was previously derived in many other contexts \([3,7,9]\).
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**Shear modulus.** – In eq. (8b), we identified the shear modulus $G$ in the free energy. As one would expect, it vanishes in the liquid phase ($\mu^2 < 1$). In the solid phase ($\mu^2 > 1$), it increases linearly with particle density $n_0$ and depends only on the cross-link density, given the gel fraction $Q = Q(\mu^2)$.

Close to the gel transition $\mu^2 \gtrsim 1$, the shear modulus can be expanded in terms of $\epsilon := \mu^2 - 1$, resulting in power law behavior (see fig. 3a):

$$G = \frac{2}{3} n_0 k_B T \epsilon^3 + O(\epsilon^4).$$

(9)

For the highly cross-linked regime, the shear modulus can be expanded in a series in $\mu^2 e^{-\mu^2}$,

$$\frac{G}{n_0 k_B T} = \frac{\mu^2}{2} - 1 + e^{-\mu^2} \sum_{m=0}^{\infty} \frac{(m + 1)^{m-2}}{m!}(\mu^2 e^{-\mu^2})^m,$$

(10)

which actually converges for all $\mu^2 > 1$ and thus can be used to compute $G$ for all $\mu^2 > 1$. In the highly cross-linked regime $\mu^2 \gg 1$, $G$ is approximated by (see fig. 3b)

$$G = \frac{1}{2} n_0 k_B T (\mu^2 - 2) + O(e^{-\mu^2}).$$

(11)

The scaling $G \sim \epsilon^3$ close to the critical point has been derived previously [5, 6]; the critical exponent is a result of mean-field theory and expected to be modified by interacting fluctuations below $d = 6$ [11]. In the highly cross-linked limit, fluctuations are presumably weak so that our result is expected to hold even beyond the Gaussian expansion around mean-field theory. The result we get is reminiscent of the classical theory of rubber elasticity, $G = n_s k_B T$, with the density of strands $n_s$ being replaced by the density of cross-links: $\frac{1}{2} \mu^2 n_0 = [M]/V$.

In order to compare the calculated shear modulus with experimental results, note that, if the cross-link length is small compared to the particle size, it is unlikely for one monomer in $d = 3$ ($d = 2$) dimensions to be connected to more than 12 (6) other monomers. Therefore, average coordination numbers $\mu^2 > 12$ (6) are inaccessible in these systems. Only if long tethers can form, reaching further than the nearest neighbor, higher average coordination numbers $\mu^2$ are possible.
Conclusions. – We have determined the shear modulus $G$ of a randomly cross-linked system. It only depends on the particle density $n_0 = N/V$ and the average coordination number $\mu^2$. Interestingly, neither the distribution of localization lengths $P(\xi^2)$, which entered the order parameter in eq. (7), nor the typical cross-link length $a$ influence the macroscopic behavior of the material. This result is consistent with the observation that the shear modulus determines the response of the system to a shear deformation on the longest scales: The wavelength of the shear deformation has to be larger than all microscopic length scales. Furthermore, one observes that $G \sim T$, i.e. the shear elasticity is purely entropic. This is a consequence of our simple model with entropic springs to account for the cross-links. In more complex systems, e.g. covalently bonded random networks, one expects to find additional energetic contributions to $G$ in the highly cross-linked regime. In any case, the bulk modulus should depend on the strength of the excluded-volume interaction, and hence it is not expected to be as universal as the shear modulus.

We also stress that the shear modulus does not depend on the spatial dimension $d$, apart from the fact that the maximal coordination numbers depend on dimensionality and determine the physical range of $\mu^2$. Again, this could be expected, because we only consider a Gaussian expansion around the saddle point; interactions between fluctuations will most likely cause a dependence on dimensionality.

It is also of interest to study the local elasticity, i.e., the response to shear deformations of finite or even small wavelength. Random networks are strongly inhomogeneous, so that one expects the elasticity to fluctuate spatially. Work along these lines is in progress.

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REFERENCES

[10] In refs. [5,6] a slightly different Ansatz for $\Omega(\hat{x})$ was used, which was not quite correct, but gave rise to the same scaling $G \sim \hat{c}^3$.