Fluctuation-stabilized marginal networks and anomalous entropic elasticity
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The stiffness of elastic networks depends on the mechanical properties of their constituents as well as their connectivity, which can be measured by the average coordination of nodes. Maxwell showed that a network of simple springs will only become rigid once the connectivity exceeds a critical, isostatic value at which the number of constraints just balances the number of internal degrees of freedom [1]. This purely mechanical argument can be used to understand the rigidity of such diverse systems as amorphous solids [2], jammed particle packings and emulsions [3,4], and even some folded proteins [5]. Interestingly, underconstrained systems that are mechanically floppy can become rigid when thermal effects are present. Perhaps the best known example of this is entropic elasticity of flexible polymers [6]. Even a single, freely jointed chain that is mechanically entirely floppy becomes elastic at finite temperature $T$: such chains resist extension with a spring constant that is proportional to $T$. At the level of networks of such chains, the macroscopic shear modulus also grows proportional to $T$ [6,7]. Many systems, including network glasses [8–10] and some biopolymer networks [11–13], can be considered intermediate between a purely mechanical regime well above the isostatic point and a purely thermal or entropic regime below the isostatic point. However, very little is known about thermal effects in such systems near the isostatic point [14–17].

Here, we show that simple model networks, consisting of randomly diluted springs, can be stabilized by thermal fluctuations, even at low connectivity for which they would be floppy at zero temperature. Interestingly, we find that the linear shear modulus $G$ exhibits anomalous temperature dependence both at and below the isostatic point. Specifically, we find that $G \approx T^\alpha$, where $\alpha < 1$. This is surprising since one might have expected, in analogy with freely jointed chains, that such networks would exhibit ordinary entropic elasticity ($G \approx T$) below the isostatic point, as the mechanically floppy modes are excited thermally. Moreover, we find two distinct anomalous entropic elasticity regimes in the connectivity-temperature phase diagram, with the Maxwell isostatic point acting as a zero-temperature critical point (Fig. 1).

We perform Monte Carlo (MC) simulations on 2D spring networks that consist of $N = n^2$ nodes, arranged on a triangular lattice, that are connected by $N_{sp} = zN/2$ springs, where $z$ is the average connectivity ($z = 6$ for the fully connected network). Periodic boundary conditions are used in all directions. To avoid network collapse [18], we consider two cases: one in which we keep the system area $A$ fixed and treat the springs as “phantom” (i.e., we ignore steric interactions, and hence the springs are potentially overlapping), and one where we fix the system pressure $P$ and prevent the springs from overlapping (self-avoiding springs). In both cases, the system energy is given by

$$\text{FIG. 1 (color online). Schematic phase diagram of thermal networks in the } T - z \text{ representation, where “reduced } T \text{” is the ratio of the temperature to the spring energy and } z \text{ is the connectivity, with critical connectivity } z_c. \text{ Reminiscent of quantum-critical points [39,40], we find a critical regime that broadens out for temperatures above the } T = 0 \text{ critical point.}$$
The network shear modulus $G$ in units of $k_{sp}$ for $N = 3600$ nodes connected by phantom springs of rest length $\ell_0 = 1$. The main plots are for a fixed area $A = A_0$, the area of a relaxed, fully connected network at $T = 0$. The corresponding results for self-avoiding springs at $P = 0$ are shown in the insets. (a) $G$ as a function of $z$ for $T = k_B T / k_{sp} \ell_0^2 = 10^{-6}$ (lower), $10^{-4}$, $10^{-3}$, $10^{-2}$, $10^{-1}$, and 1 (upper). The solid line shows $T = 0$ results. (b) $G$ as a function of $T^*$ for $z = 6$ (triangles), $z = 3.857 \approx z_c$ (circles), and $z = 3$ (squares). (c) Scaling of the shear modulus using the form $G = k_{sp} / G(T^*/|\Delta z|^b)$, where $\Delta z = z - z_c$, for $T^* < 10^{-5}$. The two branches on the left-hand side correspond to $z > z_c$ (upper) and $z < z_c$ (lower). In both systems, the asymptotes and exponents $(a = 1.4$ and $b = 2.8$) are the same.

$$U = \frac{k_{sp}}{2} \sum_{i=1}^{N_q} (\ell_i - \ell_0)^2,$$

where $\ell_i$ is the length of spring $i$, $\ell_0$ is the rest length, and $k_{sp}$ is the spring constant. In order to lower the connectivity of the system, we set $k_{sp} = 0$ for randomly chosen springs. For the phantom network, this is identical to removing springs, while for the self-avoiding network, this method has the advantage of computational efficiency over simply removing the springs, since springs with $k_{sp} = 0$ still contribute steric interactions and hence the nodes are essentially confined to a “cell” by the surrounding springs.

To find the critical (isostatic) point $z_c$, for the onset of rigidity at $T = 0$, we use a conjugate gradient algorithm to calculate $G$. For 2D networks, $z_c \approx 4$ [1,9], although due to finite size effects this will be somewhat smaller for each $N$ value studied [20]. We then increase $T$ in steps and allow the systems to equilibrate using MC simulations, obtaining configurations under shear. We note that there is an additional critical point $z_p \approx 2.084$ [21], corresponding to the connectivity percolation threshold, below which there is no connected path through the network. For $T > 0$, the shear modulus is finite between $z_p$ and $z_c$ [16].

In order to shear the systems, we use Lees-Edwards boundary conditions [22] to apply a shear strain $\gamma$. The shear modulus $G$ is then given by

$$G = \frac{1}{A} \frac{\partial^2 \mathcal{F}}{\partial \gamma^2},$$

where $\mathcal{F}$ is the free energy of the system. It is not possible to directly calculate $\mathcal{F}$ from MC simulations, so we calculate the linear shear modulus $G$ as described in Refs. [23,24]. Moreover, since $G$ has units of $k_{sp}$ in 2D, we express $G$ throughout in units of $k_{sp}$.

At low temperatures, we find that the shear modulus closely follows the zero-temperature behavior, decreasing as $z$ is decreased from the fully connected network, in both phantom and self-avoiding networks [Fig. 2(a)]. Below the critical point $z_c$, we find that the shear modulus deviates from the zero-temperature behavior, becoming nonzero for all finite temperatures. For $z > z_c$, the shear modulus is largely insensitive to temperature, while for $z < z_c$, $G$ depends strongly on $T$. For high temperatures, the shear modulus becomes increasingly insensitive to $z$ and deviates from the zero-temperature behavior at increasingly high connectivities above $z_c$, until eventually, when $k_BT - k_{sp} \ell_0^2$ (where $k_B$ is the Boltzmann constant), the thermal energy of the system is such that the network structure becomes unimportant.

The different regimes of the dependence of $G$ on $T$ can be seen in Fig. 2(b). At high connectivities, the shear modulus remains almost constant as the temperature is increased, rising only as the thermal energy $k_BT$ approaches the spring energy $k_{sp} \ell_0^2$. As we approach the critical point, however, we find that the shear modulus, which will be 0 at $T = 0$, shows an approximate $T^{1/2}$ dependence at low temperatures. This anomalous temperature dependence is apparent over many orders of magnitude and in fact corresponds to the system becoming stiffer than expected at low $T$ for ordinary entropic elasticity. As we increase the temperature further, in the self-avoiding spring networks, we see this $T^{1/2}$ dependence give way to linear $T$ dependence, while in the phantom spring networks, we see a steeper $T$ dependence, although it does not become linear. For $z < z_c$, we find another anomalous regime with $G \propto T^\alpha$, where $\alpha \approx 0.8$, at low temperature, followed by linear $T$ dependence at high temperatures in both phantom and self-avoiding networks. As we see these anomalous regimes in both types of network, we conclude
that they are not driven by steric interactions but instead by the random network structure of these low z value systems. Consistent with this, if we remove bonds in such a way as to leave one-dimensional chains of springs (i.e., chains with \( z = 2 \)) or honeycomb lattices (with \( z = 3 \)), we find \( G \propto T \) even at low temperatures, as one would expect for ordinary entropic elasticity [24].

The observed shear moduli can be well described by a scaling form analogous to that of the conductivity of a random resistor network [25] that has also been successfully used to describe the shear moduli of athermal spring and fiber networks [20,26]. For our system, this scaling ansatz is given by

\[
G = k_{sp} |\Delta z|^a \mathcal{F}(T^*|\Delta z|^{-b}),
\]

where \( a \) and \( b \) are constants, \( \Delta z = z - z_c \), and the function \( \mathcal{F} \) is dimensionless, as is its argument. We find the best collapse of the data at low temperatures (\( T^* = k_B T / k_{sp} \ell_0^2 < 10^{-5} \)) for both the self-avoiding and phantom networks using the exponents \( a = 1.4 \) and \( b = 2.8 \), as shown in Fig. 2(c). This again demonstrates the three low-temperature regimes, with almost constant \( G \) for \( z > z_c \), \( G \) scaling with \( k_{sp} T^{-0.8} (\sim k_{sp}^2 T^{-0.8}) \) for \( z < z_c \), and \( G \) showing \( k_{sp} T^{-1/2} (\sim k_{sp}^2 T^{-1/2}) \) dependence as \( \Delta z \to 0 \). We note that, similar to our findings, a recent study of athermal fiber networks in two dimensions, with both filament stretching described by \( k_{sp} \) and bond bending described by stiffness \( \kappa \), found that the shear modulus scales with \( k_{sp}^{1/2} \kappa^{1/2} \) at the critical connectivity [20].

The nonzero shear modulus we find below \( z_c \) can be shown to be entropic in origin. The shear modulus can be broken down into its energetic and entropic parts as

\[
G = \frac{1}{\lambda} \left( \frac{\partial^2 U}{\partial \gamma^2} - T \frac{\partial^2 S}{\partial \gamma^2} \right) = G_E + G_S,
\]

where \( S \) is the entropy, and both \( G_E \) and \( G_S \) can be calculated during our simulation runs [24]. We first show the ratio \( G_S/G \) versus \( z \) for the phantom networks in Fig. 3(a). At low temperature, we see that \( G_S/G \) rises sharply as \( z \) approaches \( z_c \) from above, before saturating to \( G_S/G \approx 1 \) below \( z_c \), corresponding to a dominant entropic contribution. For \( z > z_c \), the energetic contribution \( G_E \) dominates, although \( G_S \) becomes increasingly important at higher \( T \).

Figure 3(a) suggests that the behavior below the critical point can be understood in terms of \( G_S/G \) alone. Thus, when considering the origins of the anomalously temperature dependence of the shear modulus observed in Fig. 2, it is instructive to look at the behavior of \( \partial^2 S / \partial \gamma^2 \) with temperature and connectivity. From Eq. (4), it can be seen that for pure entropic elasticity (where \( G \propto T \)), we should see \( \partial^2 S / \partial \gamma^2 \propto T^0 \). In Fig. 3(b), we show \( G_S/T^* \) against connectivity for a range of temperatures in a system of phantom springs at constant area. As can be seen, \( G_S/T^* \) diverges at low temperatures as the critical point is approached, both from above and below \( z_c \). In Fig. 4(a), we show \( G_S/T^* \) versus temperature. At the critical point, we observe that \( G_S/T^* \propto T^{-1/2} \) at low temperatures. Similarly, for \( z = 3 < z_c \), we find that the low temperature \( G_S/T^* \propto T^{-0.2} \), before becoming approximately constant at higher temperatures \( (G_S/T^* \propto T^0) \). The high value of \( \partial^2 S / \partial \gamma^2 \) at low temperatures corresponds to the entropy decreasing more rapidly as the system is sheared. As noted previously, for honeycomb-like lattices and ideal chains we find ordinary entropic elasticity, corresponding to \( G_S/T^* \propto T^0 \) throughout [24].

Hence, we conclude that the anomalous dependence of the entropy on shear strain \( \gamma \) at low temperatures arises from the disordered nature of the network, leading to the anomalous temperature dependence of the shear modulus. We note that we see qualitatively similar behavior of \( G_S/T^* \) with \( T \) at low temperature for self-avoiding networks, as one would expect from Fig. 2(b).

A possible origin of this anomalous temperature behavior in subcritical networks could be the internal stress \( \sigma_I \) of the network, which in the phantom networks arises from the resistance to the tension the network is placed under in order to maintain its area. This tension can be shown to be proportional to the temperature [24]. As such, at low temperatures, the shear modulus can be expected, on
dimensional grounds, to scale as \( G \propto \sigma_0^\alpha k_{sp}^{1-\alpha} \), which would appear as \( G \propto T^\alpha k_{sp}^{1-\alpha} \) in our simulations. A similar anomalous dependence on stress was found in athermal networks with disordered molecular motors in Ref. [27]. Interestingly, if one takes the spring constant \( k_{sp} \) to be proportional to \( T \), as would be expected for freely joined chains linking nodes, then pure entropic elasticity would be recovered, with \( G \propto T \) and \( \sigma^2 / \gamma^2 \propto T^0 \). However, if \( k_{sp} = cT \), where \( c \) is a constant, it follows from Fig. 4(a) that the gradient of \( G \) with \( T \) would depend on the value of \( c \). In Fig. 4(b), we show the shear modulus against temperature for networks with \( z = 3 \) and \( k_{sp} = cT \), using a range of \( c \) values. Although all the systems show linear \( T \) dependence, we do see that as \( c \) decreases, the shear modulus becomes smaller, until \( c \approx 10^2 \), where the results converge.

Our results demonstrate that there are two distinct regimes with anomalous temperature dependence of the shear modulus, as illustrated in Fig. 1. In both cases, the dependence on \( T \) is sublinear. Thus, at low temperatures, this corresponds to an anomalously large effect of thermal fluctuations. The natural energy scale in our model is the spring energy \( k_{sp} \gamma^2 \), which can easily be much larger than the thermal energy, even at room temperature. For protein biopolymers, for instance, it is expected that \( k_{sp} \approx E d^2 / \ell_0 \), where the diameter \( d \) is of the order of nanometers and the Young’s modulus \( E \) can be as large as 1 GPa [28,29], and hence the spring energy for a segment of length \( \ell_0 \approx 100 \text{ nm} \) can be more than \( 10^6 \) times larger than \( k_B T \) at room temperature [30]. Hence, for such systems, reduced temperatures \( T' \) in the range \( \approx 10^{-6} \) can be relevant and network-level thermal fluctuations can be much larger than expected based on naive entropic estimates. Importantly, such network-level fluctuations are almost always ignored in prior fiber network models and simulations, where either purely mechanical models [20,26,34–36] or hybrid mechanical models that include only single-filament fluctuations [37,38] have been used. Finally, it is interesting to note that our phase diagram in Fig. 1 is reminiscent of other systems with zero-temperature critical behavior, such as quantum-critical points [39,40]. As in such systems, in which the critical point is also governed by fluctuations other than thermal, we find a broad critical regime that fans out and extends for temperatures potentially far above \( T = 0 \).

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[30] In the case of semiflexible polymers, thermal fluctuations can lead to a reduced longitudinal spring constant, as well as a different $T$ dependence. This mechanical estimate is valid, however, for biopolymers of stiffness comparable to or greater than that of $F$ actin. Taking the spring constant to be thermal rather than mechanical, using $k_{sp} = 90k_BT_p/\ell^4$, a value of $T_p < 10^{-6}$ is again found at room temperature (using values for the persistence length of $\ell_p \sim 10 \mu$m and the contour length of $\ell_c \sim 10$ nm) [33].