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 $G \propto T^\alpha$, 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 ($G \propto T$) 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

$$E = k_B T \sum_{i} \log \left( 1 - \frac{r_i}{l_i} \right) + \frac{1}{2} k \sum_{i<j} \left( \frac{r_{ij}}{l_{ij}} \right)^2$$

where $r_i$ is the length of the $i$th spring, $l_i$ is its equilibrium length, $k_B$ is the Boltzmann constant, $k$ is the spring constant, and $P$ is the system pressure.
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.

\[ \mathcal{U} = k_{sp} \sum_{i=1}^{N_u} (\ell_i - \ell_0)^2, \]

(1)

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, $z_c = 4$ [19,20], 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

\[ G = \frac{1}{A} \frac{\partial^2 \mathcal{F}}{\partial \gamma^2}. \]

(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

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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 success-
fully used to describe the shear moduli of athermal spring
and fiber networks [20, 26]. For our system, this scaling
ansatz is given by

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

(3)

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 ($T^* = k_BT/k_{sp} \ell_0^2 < 10^{-5}$) 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 $k_{sp} T^{0.8} \sim k_{sp} T^{0.8}$ for $z < z_c$
and $G$ showing $k_{sp} T^{1.2} \sim k_{sp} T^{1.2}$ 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 $k_{sp} \kappa^{1/2}$ 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

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

(4)

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 $G_S$ alone. Thus, when
considering the origins of the anomalous temperature de-
pendence 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 $G_S/T^*$
$= -k_{sp} \ell_0^2 (\partial^2 S/\partial \gamma^2)/k_BT$ against connectivity for a range of
networks in a system of phantom springs at constant

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{(color online). (a) The ratio $G_S/G$ as a function of
$\Delta z$ for a phantom network at $T^* = k_BT/k_{sp} \ell_0^2$.
(b) $G_S/T^* = -k_{sp} \ell_0^2 (\partial^2 S/\partial \gamma^2)/k_BT$ (units of $k_{sp}$) as a function
of $\Delta z$ for the same systems as above. Results are for $A = A_0$,
$N = 3600$, and $\ell_0 = 1$.}
\end{figure}

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 $G_S/T^* \propto T^{-2}$, 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-
lattice-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 anom-
alous 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 \( G \propto \sigma_0^2 k_{sp}^{-a} \), which would appear as \( G \propto T^a k_{sp}^{-a} \) 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 \( \partial^2 S / \partial \gamma^2 \propto T^0 \). 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 \( c \leq 10^2 \), 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 \( k_{sp} \ell_0^2 \), which can easily be much larger than the thermal energy, even at room temperature. For protein biopolymers, for instance, it is expected that \( k_{sp} \approx Ed^2 / \ell_0 \), 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 \( k_BT \) at room temperature \([30]\). Hence, for such systems, reduced temperatures \( T^* \) in the range \( \leq 10^{-6} \) 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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In the case of semiflexible polymers, thermal fluctuations can lead to a reduced longitudinal spring constant, as well as a different $T$ dependence [11,31,32]. 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 $k_{sp} = 90k_BT_p/\ell_p^2$, a value of $T' < 10^{-6}$ is again found at room temperature (using values for the persistence length of $\ell_p \approx 10 \mu m$ and the contour length of $\ell_c \approx 10 \text{ nm}$) [33].


