Negative Energetic Elasticity of Lattice Polymer Chain in Solvent

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Negative internal energetic contribution to elastic modulus (negative energetic elasticity) has recently been observed in polymer gels. This finding challenges the conventional notion that the elastic moduli of rubberlike materials have been investigated experimentally and theoretically. The simplest theoretical explanations for entropic elasticity are provided by statistical models of ideal chains, which are described in textbooks on thermodynamics, statistical mechanics, polymer physics, and soft matter physics.

In general, rubberlike materials composed of polymer chains exhibit an interplay between entropic ($G_S$) and energetic ($G_U$) contributions to the elastic modulus ($G$), although $G_U$ is usually much smaller than $G_S$. The energetic contributions of such materials have been conventionally considered to originate from the conformational change of polymer chains and have been theoretically modeled (e.g., the rotational isometric state model) in accordance with that notion. However, the significant negative energetic contributions $G_U$ that originate from attractive polymer–solvent interaction was recently observed in a rubberlike polymer gel, which is a chemically crosslinked polymer network containing a large amount of solvent. In this case, $G_U$ is much larger than that of the entropic energetic elasticity originating from the conformational changes, and the absolute value of $G_U$ reaches the same order of magnitude as that of the entropic elasticity $G_S$, as shown in Fig. 1(a).

Although previous studies have demonstrated the existence of negative energetic elasticity, there remains a question regarding how this quantity depends on the observed temperature. The temperature dependence of the shear modulus $G$ obtained from Refs. 10, 12, are shown in Fig. 1(a). The conditions of these experiments were the same, excluding the temperature ranges; Ref. 10 used $T = 278–298$ K, whereas Ref. 12 used $T = 288–308$ K. The values of $T^*_U$, which is the $T$-intercept of the fitted line of $G$, in Ref. 12 were shifted to values higher than those in Ref. 10. These results

![Diagram](https://example.com/diagram.png)

**FIG. 1.** Comparison between experimental results for a polymer gel and theoretical results of lattice polymer chain model (for $n = 20, r = 10a$). (a) Temperature dependence of shear modulus $G$ of the polymer gel for $T = 278–308$ K, including the midpoint $T^* = 293$ K [seven points, including the orange point ($G^*$) in the center], which are obtained from Refs. 10, 12. The tangent (dotted line) of the fitted quadratic curve (solid curve) of the points intersects with the horizontal axis at $T^*_U > 0$ and vertical axis at $G^* < 0$. Temperature dependencies of $G_U$ (pink dashed curve) and $G_S$ (blue dashed curve) are calculated from the fitted quadratic curve. (b) Temperature dependence of stiffness ($\hat{k}$) and its energetic ($\hat{k}_U$) and entropic ($\hat{k}_S$) contributions. The tangent (dotted line) of $\hat{k}$ at $\hat{T}^*$ intersects with the horizontal axis at $\hat{T}^*_U > 0$ and vertical axis at $\hat{k}^*_U \equiv \hat{k}_U(r, \hat{T}^*) < 0$. 

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imply that $G$ is an increasing convex function of $T$, and that $T_c^R$ depends on the observed temperature. However, the microscopic origin of these temperature dependencies is unknown.

In this Letter, we theoretically demonstrate the occurrence of negative energetic elasticity in a lattice polymer chain model and provide a possible explanation for the temperature dependence of $T_c^R$ observed in polymer-gel experiments [Fig. 1(b)]. We also show that the model provides a microscopic mechanism of the emergence of negative energetic elasticity by focusing on the local stiffnesses of chains.

**Lattice polymer chain model.**—We consider Orr’s polymer chain model for highly dilute polymer solutions on a simple cubic lattice with a lattice spacing $a$ [13], which is one of the simplest ways to express the interaction between a polymer chain and solvent molecules. As shown in Fig. 2(a), this model consists of solvent molecules and a polymer chain modeled based on an $n$-step self-avoiding walk [14, 15], which has one of the simplest ways to express the interaction between a polymer chain and solvent molecules. As shown in Fig. 2(b), which is known as an interacting self-avoiding walk [14, 15], which has one of the simplest ways to express the interaction between a polymer chain and solvent molecules. As shown in Fig. 2(b), which is known as an interacting self-avoiding walk [14, 15], which has one of the simplest ways to express the interaction between a polymer chain and solvent molecules.

The energy function of the model is given by

$$E^{\text{tot}}(\omega) = \varepsilon_{pp} m_{pp}(\omega) + \varepsilon_{ps} m_{ps}(\omega) + \varepsilon_{ss} m_{ss}(\omega), \quad (1)$$

where $\omega$ denotes the configuration of self-avoiding walks, and $m_{pp}(\omega)$, $m_{ps}(\omega)$, and $m_{ss}(\omega)$ are the numbers of the polymer–polymer, polymer–solvent, and solvent–solvent contact pairs, respectively. Here, the interaction energies acting between each pair are $\varepsilon_{pp}$, $\varepsilon_{ps}$, and $\varepsilon_{ss}$, respectively. Note that there is no energetic term in Eq. (1) for the conformation of $\omega$ (e.g., the angle of consecutive bonds). Once the entire lattice size is given, the total number of contact pairs, $m_{pp}(\omega) + m_{ps}(\omega) + m_{ss}(\omega)$, is constant. In addition, we can obtain $2m_{pp}(\omega) + m_{ps}(\omega) = 4n + 2$ by counting the number of solvent molecules surrounding $\omega$. Thus, when $n$ is given, Eq. (1) is rewritten as the following energy function, where the constant term has been excluded:

$$E(\omega) = \varepsilon m(\omega), \quad (2)$$

where $\varepsilon = \varepsilon_{pp} - 2\varepsilon_{ps} + \varepsilon_{ss}$, and $m(\omega) = m_{pp}(\omega)$.

Here, the original model shown in Fig. 2(a) was reduced to a single-chain system, with the intrachain interaction shown in Fig. 2(b), which is known as an interacting self-avoiding walk [14]. In the case of $\varepsilon = 0$, this model corresponds to the (noninteracting) self-avoiding walk.

Many studies on the interacting self-avoiding walk have focused on the self-attractive condition ($\varepsilon < 0$) to investigate the collapsing transition [17, 21]. By contrast, this study focuses mainly on the self-repulsive condition ($\varepsilon > 0$) to investigate the effect of attractive polymer–solvent interactions, which has been suggested as the possible microscopic origin of negative energetic elasticity [10].

**Energetic and entropic elasticity in lattice polymer chain.**—To calculate the stiffness (a single-chain counterpart of the elastic modulus) of the lattice polymer chain model, $\omega$ is considered with an on-axis constraint, where the length and direction of the end-to-end vector are $r$ and the $x$-axis, respectively (Fig. 2). Based on Eq. (2) the partition function of the model with the on-axis constraint is given by

$$Z(r, T) = \sum_{m=0}^{2n} W_{n,m}(r) e^{-\varepsilon m/(k_B T)}, \quad (3)$$

where $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. Here, $W_{n,m}(r)$ is the number of possible $\omega$ for a given set of $n$, $r$, and $m$; and $W_{n,m}(r) = 0$ for $m \geq 2n + 1$. The corresponding free energy is $A(r, T) = -k_B T \ln Z(r, T)$.

We define the stiffness of the lattice chain with the on-axis constraint. In the continuum limit ($n \to \infty$ and lattice spacing $a \to 0$), the stiffness is defined as the second derivative of the free energy:

$$k(r, T) \equiv \frac{\partial^2 A(r, T)}{\partial r^2} = k_B T \left[ \frac{\partial^2 Z(r, T)}{Z(r, T)} - \frac{\partial Z(r, T)}{Z(r, T)} \right]^2. \quad (4)$$

Thus, we define the stiffness of the lattice chain in the finite difference form as

$$k(r, T) \equiv k_B T \left[ \frac{1}{Z(r, T)} \sum_{m=0}^{2n} \frac{\Delta W_{n,m}(r)}{\Delta r} e^{-\varepsilon m/(k_B T)} \right]^2 - \frac{1}{Z(r, T)} \sum_{m=0}^{2n} \frac{\Delta^2 W_{n,m}(r)}{\Delta r^2} e^{-\varepsilon m/(k_B T)} \right], \quad (5)$$

FIG. 2. Lattice polymer chain models with on-axis constraint on end-to-end vector. (a) Two-component model of single polymer chain (open and filled black circles connected with lines) and solvent molecules (light-blue filled circles) on a lattice. There are three types of nearest-neighbor interactions. (b) Mathematically equivalent reduced model of two-component model shown in (a). (c) Example of interacting self-avoiding walk on cubic lattice with on-axis constraint.
where the first- and second-order differences of \( W_{n,m}(r) \) are given by \( \Delta W_{n,m}(r) = [W_{n,m}(r + \Delta r) - W_{n,m}(r - \Delta r)]/2 \), and \( \Delta^2 W_{n,m}(r) = W_{n,m}(r + \Delta r) - 2W_{n,m}(r) + W_{n,m}(r - \Delta r) \), respectively. Here, \( \Delta r = 2a \) because \( \omega \) exists only for odd \( \tilde{r} \equiv r/a \) for odd \( n \) and only for even \( \tilde{r} \) for even \( n \).

We decompose the elasticity into its energetic and entropic contributions as \( \kappa = \kappa_U + \kappa_S \) in the same way as in Refs. [10, 11]. According to thermodynamics, \( A = U - TS \), where \( U \) is the internal energy, and \( S \) is the entropy. Thus, in the continuum limit, the energetic and entropic contributions are \( k_U(r, T) = \partial^2 U(r, T)/\partial r^2 \) and \( k_S(r, T) = -T \partial^2 S(r)/\partial r^2 \), respectively. From Maxwell’s relation, we have \( k_S(r, T) = T \partial k(r, T)/\partial T \). In the lattice polymer chain model, we calculate \( k_S(r, T) = T \partial k(r, T)/\partial T \) and \( k_U = k - k_S \) from Eq. 5.

Results of exact enumeration. We exactly enumerate \( W_{n,m}(r) \) for \( 1 \leq n \leq 20 \) using the simplest recursive algorithm [22] with two pruning algorithms considering the octahedral symmetry of the simple cubic lattice and the reachability of \( \omega \) to a specific endpoint. Those lists are consistent with the results reported in Refs. [13, 23–32].

Occurrence of negative energetic elasticity. From the lists of \( W_{n,m}(r) \), we can calculate exact values of \( k, k_U \), and \( k_S \). Figure 1(b) illustrates the results for \( \varepsilon > 0 \), \( n = 20 \), and \( r = 10a \) by introducing the dimensionless quantities \( k \equiv \alpha^2 k/\varepsilon, k_U \equiv \alpha^2 k_U/\varepsilon, k_S \equiv \alpha^2 k_S/\varepsilon, \) and \( \hat{T} \equiv k_B T/\varepsilon \). A configuration of \( \omega \) with the same \( n \) and \( r \) is shown in Fig. 2(c) as an example. Figure 1(b) demonstrates the occurrence of negative energetic elasticity \( \hat{k}_U < 0 \) for a single lattice polymer chain in a solvent.

In Fig. 1(a), we show the previous experimental results for the shear modulus \( G \) of the poly(ethylene glycol) (PEG) hydrogel [10, 12], for comparison with our results. Figures 1(a) and (b) demonstrate the qualitative consistency between our results and those of the polymer-gel experiment. These results suggest that the mechanism of negative energetic elasticity in the polymer gel originates from a single chain. Furthermore, these results indicate the possible emergence of negative energetic elasticity in various chemically crosslinked polymer gels other than the PEG hydrogel because the simple lattice polymer chain model, not including the chemical details, qualitatively explained the polymer-gel experiment.

To examine the effect of the sign of \( \varepsilon \) on the energetic elasticity, we show the dependence of the temperature-scaled stiffness \( \hat{k}/\hat{T} = \alpha^2 k/(k_B T) \) on \( 1/\hat{T} \equiv \varepsilon/(k_B T) \) in Fig. 3 [Note that \( \hat{k}, \hat{k}_U \), and \( \hat{k}_S \) diverge for \( \varepsilon = 0 \) (noninteracting self-avoiding walk), whereas \( \hat{k}/\hat{T}, k_U/\hat{T} \), and \( \hat{k}_S/\hat{T} \) do not.] Figure 3 shows that the energetic contributions are negative, zero, and positive for \( \varepsilon > 0 \), \( \varepsilon = 0 \), and \( \varepsilon > 0 \), respectively, for \( n = 20 \) and \( r = 10a \).

As shown in Fig. 1(b), \( \hat{T}_U^* \equiv \hat{T}_U(\varepsilon^*) \) denotes the \( \hat{T} \)-intercept of the tangent of \( \hat{k} = \hat{k}(\hat{T}) \) at the reference temperature \( \hat{T} = \varepsilon^* \). For polymer gels [10, 11], \( \hat{T}_U^* \) [Fig. 1(a)] is a key factor in the analysis of negative energetic elasticity. In addition, in the lattice polymer chain model, \( \hat{T}_U \) is a better measure of negative energetic elasticity than \( k_U \) because \( \hat{T}_U^* = \varepsilon \hat{T}_U^*/k_B \) is independent of the lattice spacing \( \alpha \), in contrast to \( k_U = \hat{k}_U/\alpha^2 \), which depends on \( \alpha \).

We define \( \hat{T}_U^\infty \equiv \lim_{r \to -\infty} \hat{T}_U(\varepsilon^*) \), which is a good indicator of the negative energetic elasticity in the sense that \( \hat{T}_U^\infty > 0 \) is identical to \( k_U < 0 \) in the case of \( \varepsilon > 0 \). As shown in Fig. 3, the \( 1/\hat{T} \)-intercept of the tangent of \( \hat{k}/\hat{T} \) at \( 1/\hat{T} = 0 \) corresponds to \( 1/\hat{T}_U^\infty \). Note that \( \hat{T}_U^\infty \) is a functional of \( W_{n,m}(r) \) and is a rational number for a given set of \( n, r, \) and \( m \). In Fig. 4(a), we plot \( \hat{T}_U^\infty \) as calculated from \( W_{n,m}(r) \).

We successfully determine the analytic expressions of \( \hat{T}_U^\infty \) as rational functions of \( n \) for \( r = (n - 2)a, (n - 4)a, \) and \( (n - 6)a \), using \( W_{n,m}(r) \) up to \( n = 20 \), with additional results up to \( n = 26 \) for \( r = (n - 8)a \). For example,

\[
\hat{T}_U^\infty(n, (n - 2)a) = \frac{4(15n^8 - 356n^7 + 3766n^6 - 23016n^5 + 88019n^4 - 213804n^3 + 317784n^2 - 256008n + 81484)}{(n - 1)(9n^8 - 204n^7 + 2026n^6 - 11648n^5 + 42733n^4 - 102444n^3 + 156272n^2 - 137656n + 53028)}.
\]
In Fig. 4(b), we plot $T_{\infty}^\alpha$ as a function of $(n - \hat{r})^\alpha/n$ for $\alpha = 3/4$. Here, the three curves of the analytic expressions and the points collapse onto a single master curve, except for small values of $n$. This collapse suggests that $T_{\infty}^\alpha$ can be finite and positive for all $n \geq 6$, even in the continuum limit of $n \to \infty$ with the constraint $(n - \hat{r})^\alpha/n = \text{const}$. Thus, negative energetic elasticity will exist for all finite $n \geq 6$ and the continuum limit. Although the physical meaning of the exponent $\alpha = 3/4$ is a subject for future research, a possible explanation is that the on-axis constraint on the end-to-end vector reduces the dimensionality from three to two, resulting in the universal critical exponent $\nu = 3/4$ of the two-dimensional self-avoiding walk.  

Microscopic mechanism of negative energetic elasticity.—To characterize the microscopic properties of the lattice polymer chain with a negative $k_U$, we define a thermal average of the mean straight path length as

$$\ell(r, T) = \frac{1}{Z(r, T)} \sum_{m=0}^{2n} \sum_{b=0}^{n-1} \frac{n a}{b + 1} W_{n,m,b}(r) e^{-\varepsilon m / (k_B T)},$$

where $b$ is the number of bending points of $\omega$ and $W_{n,m,b}(r)$ is the number of $\omega$ for a given set of $n$, $r$, $m$, and $b$. In Eq. (7), $na/(b + 1)$ is the mean straight path length for each $\omega$. For example, $b = 4$ for $\omega$ in Fig. 4(b) and $b = 13$ for $\omega$ in Fig. 4(c).

Figure 5 shows that $\hat{k}$ and $\hat{k}/\hat{T}$ decrease with $1/\hat{T}$, whereas $\ell \equiv \ell/a$ increases with $1/T$. Here, $\hat{k}$ and $\hat{k}/\hat{T}$ characterize the global stiffness of the whole polymer chain, whereas $\hat{\ell}$ characterizes the local stiffness of the chain. Thus, there is a negative correlation between the global and local stiffnesses. Figure 5 also shows points corresponding to the self-avoiding walk ($\varepsilon \to 0$) and neighbor-avoiding walk ($\varepsilon \to \infty$). The inset of Fig. 5 shows the two curves of $\hat{A}/\hat{T}$ for the self- and neighbor-avoiding walks. The curvatures of $\hat{A}/\hat{T}$ correspond to $\hat{k}/\hat{T}$ for the self- and neighbor-avoiding walks. Thus, the curvatures of $\hat{A}/\hat{T}$ illustrate that the neighbor-avoiding walk is softer than the self-avoiding walk. These results show that polymer chains become locally stiffer because of the attractive interaction with solvent molecules, and globally softer because of the smaller curvature of free energy as a function of $\hat{r}$ in the case of $\varepsilon > 0$ and $k_U < 0$. This is the microscopic mechanism of negative energetic elasticity in the lattice chain model.

Conclusion.—We used the simplest lattice polymer chain model to explain both the energetic and entropic elasticity (Fig. 2). By exactly enumerating the model, we obtained the stiffness of the chain and its energetic and entropic contributions (Fig. 3). This result demonstrates that the negative energetic elasticity originates from the polymer–solvent interaction. The three rational functions of $T_{\infty}^\alpha$ with respect to $n$ are derived from the enumeration results (Fig. 4), revealing that negative energetic elasticity exists for all finite $n \geq 6$ and the continuum limit. We showed that the stiffness of the whole polymer chain is negatively correlated with the local stiffness of the chain (Fig. 5). In short, locally stiffer chains are globally softer. This simple lattice polymer chain model, which does not include chemical details, qualitatively reproduces the temperature dependence of

![Figure 4](image-url)

**FIG. 4.** (a) Exact values of $T_{\infty}^\alpha(n, r)$ for $5 \leq n \leq 20$ and three analytic curves for $r = (n - 2)a$, $(n - 4)a$, and $(n - 6)a$, shown as a gray dashed curve, light-green dot-dashed curve, and green solid curve, respectively. Each curve passes through all corresponding points of $T_{\infty}^\alpha$. (b) Same points and curves are plotted as functions of $(n - \hat{r})^\alpha/n$, where $\alpha = 3/4$. These collapse onto a single master curve.

![Figure 5](image-url)

**FIG. 5.** Negative correlation between global and local stiffnesses. (Top panel) Parametric curve of two functions $\hat{A}(1/\hat{T})$ and $k(1/\hat{T})$ together with two other parametric curves for $\hat{k}/\hat{T}$ and $\hat{k}/\hat{T}$ $n = 20$, $\hat{r} = 10$, $\varepsilon > 0$. (Bottom panel) Corresponding temperature-scaled curves. (Inset of top panel) $\hat{A}/\hat{T}$ for self-avoiding walk ($\varepsilon = 0$, light-blue squares) and neighbor-avoiding walk ($\varepsilon = \infty$, yellow rhombuses) as functions of $\hat{r}$. 

Self-avoiding walk (●) Interaction strength Neighbor-avoiding walk (○)
negative energetic elasticity observed in the experiments conducted on PEG hydrogel [10, 12] (Fig. 1), indicating that negative energetic elasticity would emerge in various chemically crosslinked polymer gels and single polymer chains [37–39] other than the PEG hydrogel. Therefore, this model provides a starting point for the further understanding of negative energetic elasticity in polymer chains and polymer networks in solvents.

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