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Elastic properties of a polymer chain

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We describe the results of computer simulations on a model polymer chain with excluded volume interactions in the presence of an external stretching force. For weak and moderate forces the response is linear while for strong forces the behavior is nonlinear, consistent with the non-Gaussian nature of the end-to-end vector $\vec{R}$ distribution for large R. In the vicinity of the Θ temperature the onset of nonlinearity occurs at larger forces.

I. INTRODUCTION

The elastic behavior of a single polymer chain in a good solvent is related to the general problem of rubber elasticity and to phenomena occurring in dilute polymer solutions subject to high-velocity gradients.[1-3] The single-chain problem has been studied recently using the scaling properties of the end-to-end vector distribution function $P_N(\vec{R})$ of chains with excluded volume interactions containing N links. According to scaling $P_N(\vec{R}) \sim P(X)$ where $X \equiv R/R_0(N)$ and $R_0^2(N)$ is the averaged squared end-to-end distance.[4] (It is important to note that scaling will not hold for very large R values, $R \sim Na >> R_0(N)$, where a is the link length.)

In the presence of a stretching force $\vec{f}$, e.g., an applied electric field $\vec{E}$ acting on two small charges attached to the ends of the chain, the end-to-end distribution function $P(X)$ is transformed into $P(X)\exp(\beta\vec{R}\cdot\vec{f})$ where $\beta = 1/kT$. The average value of $\langle \vec{R} \rangle$ is thus given by

$$\langle \vec{R} \rangle = \frac{\int P(X)\exp(\beta\vec{f}\cdot\vec{R})\vec{R}\, d^3X}{\int P(X)\exp(\beta\vec{f}\cdot\vec{R})\, d^3X}. \tag{1}$$

Let R_f be the component of $\vec{R}$ parallel to $\vec{f}$. Writing $X_f = R_f/R_0$ we find from Eq. (1) that $\langle X_f \rangle$ is a function of a single dimensionless variable $\eta = \beta f R_0$,

$$\langle X_f \rangle = \phi(\eta). \tag{2}$$

Quantities such as $\langle R_\perp^2 \rangle$ and $\langle \delta R_f^2 \rangle$, the mean-squared fluctuations in the components of $\vec{R}$ perpendicular and parallel to the stretching force, respectively, should follow a similar scaling property.

According to Pincus[1] and de Gennes[2] one can distinguish two stretching regimes.

A. *The weak stretching regime*. Here $\eta << 1$ and we can assume $\phi(\eta) \propto \eta$ so that

$$\langle R_f \rangle = Af\beta R_0^2, \tag{3}$$

with A some constant independent of N and η. Equation (3) is analogous to the stretch-force relationship of a random coil without excluded volume interactions. In the latter case, $R_0^2 \propto N$ and $A = \frac{1}{3}$ so that $\langle R_f \rangle \propto N$ while in a chain with excluded volume interactions R_0^2 and thus also $\langle R_f \rangle$, behaves as $N^{2\nu}$ ($\nu \sim 0.6$).

B. *The strong stretching regime*. Here $\eta > 1$ (but still $\beta f < 1/a$), and a linear relationship, $\langle R_f \rangle \propto N$, can be expected for all chains since in the strongly stretched chain excluded volume interactions between distant segments are greatly reduced. This assumption together with Eq. (2) leads to the power-law relation[4]

$$\phi(\eta) \propto \eta^{\lambda}, \quad \lambda = (1/\nu - 1) \simeq 0.66. \tag{4}$$

Assuming that for large values of X, $P(X)$ is approximately of the form

$$P(X) \propto \exp(-\text{const}X^{\delta}), \tag{4'}$$

one can use Eq. (1) to obtain $\langle R_f \rangle \propto R_0\eta^{\gamma}$ with $\gamma = 1/(\delta - 1)$. When combined with (4) this gives

$$\delta = (1-\nu)^{-1} \simeq 2.5.$$

In the present note the above theoretical considerations will be tested for the first time by numerical results obtained from Monte Carlo simulations of model chains in a continuum. We shall also present some results for the elastic properties of a polymer chain in the Θ regime when the excluded volume interactions are approximately balanced by attractive interactions.

II. THE MONTE CARLO METHOD

The model chain[5] is made up of $N+1$ beads located at positions $\{\vec{r}_i\}$, $i=0,\ldots,N$ separated by links of fixed length a. Any two beads in the chain interact via a potential $V(r_{ij})$:

$$V(r_{ij}) = \begin{cases} V_{LJ}(r_{ij}) - V_{LJ}(R_m), & r_{ij} < R_m \\ 0, & r_{ij} > R_m \end{cases} \tag{5}$$

and

$$V_{LJ}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right],$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and V_{LJ} is the Lennard-Jones potential.

Note that for $R_m = 2^{1/6}\sigma$ the potential is purely repulsive while for larger values of R_m it has a finite attractive region. It is generally believed that the behavior of long polymer chains is universal, i.e., it depends only on the general features, not the details of the interaction.

In our simulations we considered two cases: (i) purely repulsive interaction, $R_m = 2^{1/6}\sigma$, $\beta\epsilon = 0.1$, $\sigma = 0.7a$. This represents a chain in a good solvent; (ii) $R_m = 2\sigma$, $\sigma = 0.7a$ and different values of $\beta\epsilon$ including the neighborhood of the Θ point in a poor solvent. The total interaction energy for a chain configuration Y is thus given by

$$U(Y,\vec{f}) = \sum_{i>j} V(r_{ij}) - \vec{f}\cdot(\vec{r}_N - \vec{r}_0). \tag{6}$$

An ensemble of configurations distributed according to the canonical distribution

$$P(Y,\vec{f}) \propto e^{-\beta U(Y,\vec{f})}$$

was generated by a reptation Monte Carlo (MC) dynamics[6] as follows: A configuration $Y' = \{r_i'\}$ is generated from the configuration Y by the transformation

$$\begin{aligned} \vec{r}_i' &= \vec{r}_{i+1}, \quad \text{for } i = 0,\ldots,N-1, \\ \vec{r}_N' &= \vec{r}_N + \vec{s}, \quad |\vec{s}| = a, \end{aligned} \tag{7}$$

and the direction of $\vec{s}$ is chosen at random from a uniform distribution. With equal probability, this transformation is carried backwards, i.e., with $\vec{r}_i' = \vec{r}_{i-1}$ and $\vec{r}_1'$ in a random direction at a distance a from $\vec{r}_1$.

A new configuration Y_{new} of a Markov sequence is taken as either Y or Y' according to the Metropolis criterion[7]:

$$Y = \begin{cases} Y', & \text{if } \exp\{\beta[U(Y,\vec{f}) - U(Y',\vec{f})]\} > \mu \\ Y, & \text{otherwise}, \end{cases} \tag{8}$$

where μ is a random number uniform on (0, 1). This procedure obeys the detailed balance criterion, and leads asymptotically to the equilibrium distribution.

The relaxation time of the reptation dynamics is of the order of $\sim N^2$ Monte Carlo steps. Equilibrium averages are obtained by dividing the total sequence of MC steps into 15–20 blocks, each block $> N^2$, and obtaining the final average and the standard deviation by averaging over the block averages, excluding the first couple of blocks during which the system is still in the process of equilibration.

III. RESULTS AND DISCUSSION

A. *Weak stretching regime*. In Fig. 1 we plot $\langle X_f \rangle$ versus $\eta \equiv \beta f R_0$ for $\eta \le 2$. We note the linear dependence. The line in Fig. 1 represents the relation $\langle X_f \rangle = \eta/3$ which corresponds to $A = \frac{1}{3}$ in Eq. (2). Our results show that within the statistical errors (which become large for small stretching force) the linear-response law is obeyed for $\eta \lesssim 1.5$. This is considerably beyond the regime where Eq. (8) might have been expected to hold *a priori*. The fact that $A = \frac{1}{3}$ can be interpreted to imply that $P(X)$ is well approximated by a Gaussian distribution around its maximum at $X = 1$. To check this interpretation, we evaluated the fluctuations $\langle (R_f - \langle R_f \rangle)^2 \rangle$. We find that for $\beta f R \lesssim 2$, $\langle (R_f - \langle R_f \rangle)^2 \rangle \simeq R_0^2/3$ consistent with a Gaussian distribution. The relatively large statistical errors in this regime are

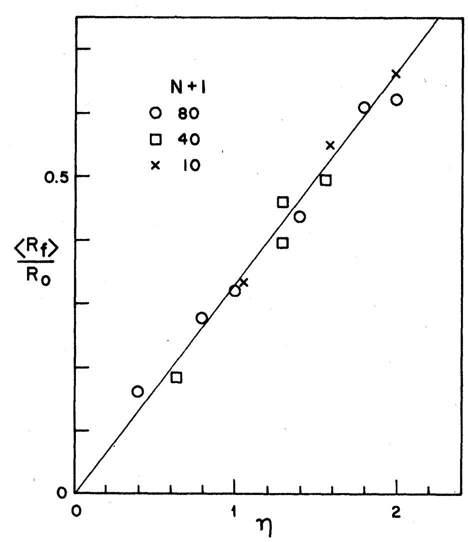

FIG. 1. The normalized average component of the end-to-end vector in the direction of the force $\langle R_f \rangle / R_0$ versus $\eta \equiv \beta f R_0$ for $\beta f R_0 < 2$. The straight line represents the relation $\langle R_f \rangle / R_0 = \frac{1}{3}\eta$.

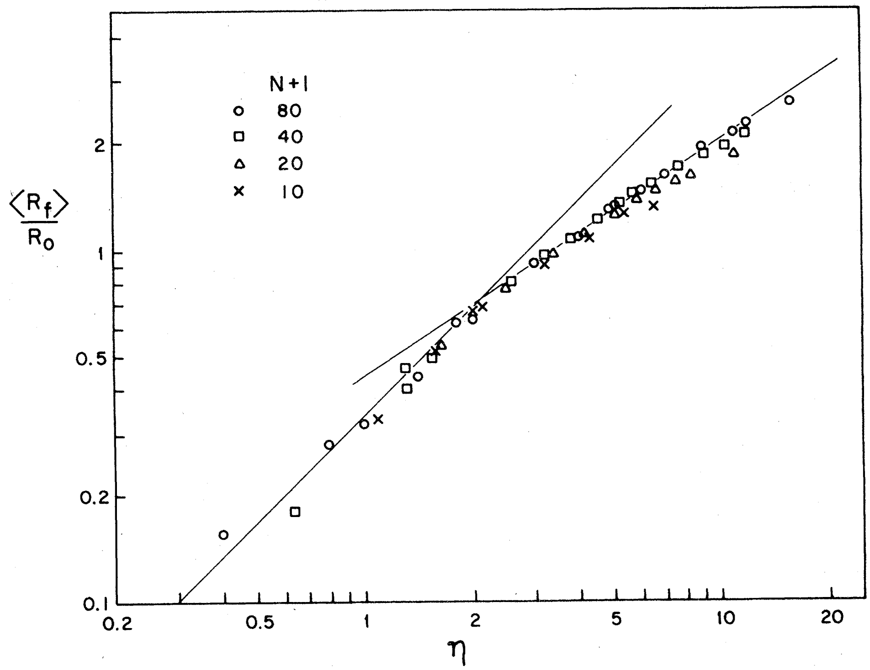

FIG. 2. Log-log plot of $\langle R_f\rangle/R_0$ versus η for chains of $N=10-80$. The straight lines represent the relations $\langle R_f\rangle/R_0 \propto \eta$ and $\langle R_f\rangle/R_0 \propto \eta^{2/3}$.

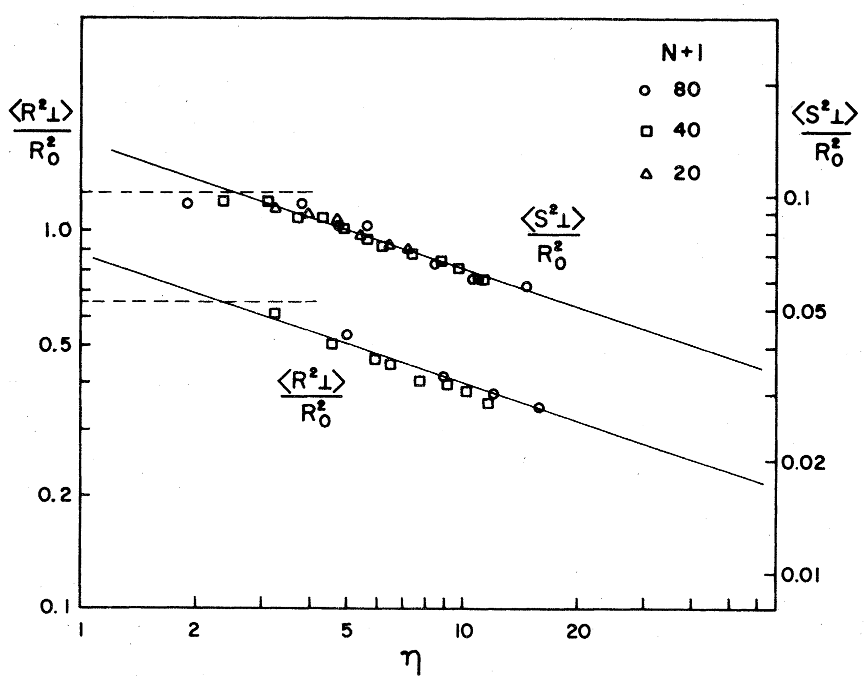

FIG. 3. The lateral extension of the stretched chain. A log-log plot of $\langle R_\perp^2\rangle/R_0^2$ versus η (the slope of the solid line: $-\frac{1}{3}$); a log-log plot of $\langle S_\perp^2\rangle/R_0^2$ versus η (the slope of the solid line: $-\frac{1}{3}$). The dashed lines represent the values of $\langle R_\perp^2\rangle/R_0^2$ and $\langle S_\perp^2\rangle/R_0$ for a free chain.

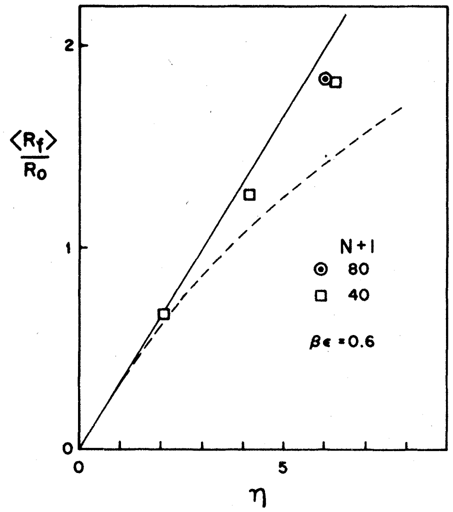

FIG. 4. The normalized average component of the end-to-end vector in the direction of the force $\langle R_f \rangle / R_0$ versus η for a chain with attractive interactions. The solid line represents $\langle R_f \rangle / R_0 = \frac{1}{3}\eta$. The dashed line represents the results for purely repulsive interactions.

due to the fact that as $\langle R_f \rangle \to 0$ for $f \to 0$, the fluctuation remains $\frac{1}{3}R_0^2$.

B. *Strong stretching regime*. Figure 2 presents the values of $\langle X_f \rangle$ versus η on a log-log plot. The straight line represents the power-law dependence, Eq. (4), with $\nu = 0.6$. The following features can be noted.

(i) For the longest chain studied $N = 80$ there is a very good fit to this power law in the range $3 \leq \eta \leq 12$. In this range $\phi(\eta) \simeq 0.43\ \eta^{0.66}$. For sufficiently large values of X and η the integrand in Eq. (1) should have the form: $\exp(-\Lambda X^\delta + \eta X_f)$. If one approximates $\langle X_f \rangle$ by X_f^0, the value of X_f for which this integrand has a maximum one obtains

$$\phi(\eta) \cong \left(\frac{1}{\Lambda^\delta}\right)^{1/(\delta-1)} \eta^{1/(\delta-1)}$$

By comparing this expression with our numerical results we estimate $\Lambda \simeq 1.2-1.4$.

(ii) For each chain length N the scaling $\langle R_f \rangle / R_0 = \phi(\eta)$ is obeyed up to a maximum value of $\eta = \eta_c(N)$ which increases with N. For $\eta > \eta_c(N)$ the results for a chain of length N show some deviation from the universal curve. It seems that $\eta_c(N)/R_0(N)$ is approximately N independent, and has the value 0.6–0.7. Thus the upper limit of the scaling regime corresponds to a $\beta f \sim 1/a$. For higher stretching forces the dependence of the elongation of f is slower than $\langle R_f \rangle \propto f^{2/3}$.

(iii) Transverse fluctuations: Figure 3 presents the effects of the stretching on the dimensions of the coil perpendicular to the direction of the stretch as characterized by $\langle R_\perp^2 \rangle$. We find that $\langle R_\perp^2 \rangle / R_0^2$ is also, roughly, a function of the single variable η. $\langle R_\perp^2 \rangle$ decreases with increasing stretch. The straight line represents the $\eta^{-0.33}$ dependence expected from scaling theory. Our results confirm this power law. Similar behavior characterizes $\langle S_\perp^2 \rangle$ the radius of gyration in a plane perpendicular to $\vec{f}$ as shown in Fig. 3. The data which characterize the perpendicular size are more noisy at large stretches than R_f.

C. *A chain with attractive interactions*. The results of $\langle X_f \rangle$ versus η for a chain with attractive interactions are represented in Fig. 4. Here the potential given by Eq. (5) with $R_m = 2\sigma$ and $\beta\epsilon \simeq 0.6$ was used. For this value of $\beta\epsilon$ the N dependence of $\langle R^2 \rangle$ in the free chain is linear, so that the temperature can be considered to be in the theta region.[8] We find indeed that the linear behavior persists over a wider range of stretching force than in the purely repulsive case, i.e., $\phi(\eta)$ is linear for $0 < \eta < 4$. This is consistent with a Guassian-type behavior of $P(X)$ extending over a wider range of X values.

CONCLUSIONS

We find that for weak and moderate stretching $f \leq 1.5/\beta R_0$ a linear-stress strain relationship holds for chains with excluded volume interactions, similar to a behavior of an ideal coil under stretching. The lateral dimensions are not sensitive to the stretching in this regime. For large stretching $\beta f > 3/R_0$ the f dependence of the elongation is nonlinear and the lateral dimensions contract with increasing f. The dependence of $\langle R_f \rangle$ and $\langle R_\perp^2 \rangle$ on f obeys power laws with exponents which agree with those predicted by scaling arguments. The basic scaling property of the magnitudes $\langle R_f \rangle / R_0$ and $\langle R_\perp^2 \rangle / R_0^2$ is obeyed in the range $0 < \beta f \lesssim 1/a$. For higher stretching forces a slower dependence of the elongation on f than $\langle R_f \rangle \sim f^{2/3}$ seems to emerge.

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