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Polymers in a Vacuum

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In a variety of situations, isolated polymer molecules are found in a vacuum, and here we examine their properties. Angular momentum conservation is shown to significantly alter the average size of a chain and its conservation is only broken slowly by thermal radiation. For an ideal chain, the time autocorrelation for monomer position oscillates with a period proportional to chain length. The oscillations and damping are analyzed in detail. Short-range repulsive interactions suppress oscillations and speed up relaxation, but stretched chains still show damped oscillatory correlations.

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The properties of polymer chains have been investigated extensively over the past 50 years [1], but the vast majority of these studies have been concerned with situations where they are in a solution or melt. However, there are some situations where polymer molecules are essentially in a vacuum. Below are some possible situations where polymers in this state might prove very interesting to investigate further.

The desorption and ionization of polymers, often by lasers, are carried out during mass spectrometry, in order to characterize proteins and have many important biological applications [2]. Such desorbed chains often carry charge and move freely through empty space. In this situation they will respond strongly to electromagnetic radiation in the frequency range of their internal dynamics, and therefore their internal properties could in this way be probed. This extra information has potential for improving this important technique.

Although at present it is difficult, it might also prove possible to use optical tweezers on biomolecules such as DNA in a vacuum, analogous to what is now done in aqueous solution, and measure the spectrum of Brownian motion [3], providing detailed information on the polymer's dynamics. Additionally it might be possible to suspend DNA over a "trench" in a manner analogous to what has been done with nanotubes [4].

Polymers of many kinds have been detected in interstellar media [5] and although they have been predominantly less than 10 units, the detection of new species requires theoretical models to fit spectroscopic data. Thus modeling longer chains is useful in this regard.

In addition, we will show that the study of polymers without solvent present sheds light on the problem of internal or Cerf friction [1,6] of polymers, a fundamental and still poorly understood phenomenon.

To aid in the possible experimental observation of such systems, some basic properties of isolated polymers in a vacuum are considered here. The first question that we ask is how their statistics are modified from those in solution. Solvents will compete with intrachain attractions so that above the θ temperature [1], a polymer chain will be swollen. Without the solvent present, this would imply that a chain at the same temperature would be collapsed. But at high enough temperatures, entropy will dominate over energy, and a polymer, just like a liquid, will then want to expand into a gas, or self-avoiding phase. Because carbon-carbon bonds are very strong, it might then be possible to find some species where a polymer will become swollen in isolation for long enough periods of time to be observable. Even if it turns out that this is not possible, polymers through desorption often carry charge, for example, in mass spectroscopy, and this additional Coulomb repulsion is quite substantial; at 500 K it is $\approx 33k_BT$ for two electrons 1 nm apart. This will serve to stretch a chain.

It might then appear that the statistics of such a system are identical to that of a chain in a solvent, with some modification of interaction parameters. However, one important difference is the conservation of angular momentum that we might expect to see in this case as opposed to a polymer in a solvent. In statistical mechanics, this conservation law is ordinarily ignored and is not expected to make a difference to system properties when the number of degrees of freedom is large. However, we will see that for a polymer in isolation it has a significant effect on its size, even when the total angular momentum is zero. The effects of angular momentum conservation have been recently studied in self-gravitating systems [7] where it leads to different phases for some models for finite angular momentum.

The starting point for this situation is the formula for the classical entropy of N monomers with coordinates $\mathbf{r}_1, \ldots, \mathbf{r}_N$ interacting with potential energy U in the microcanonical ensemble with conservation of total linear $\mathbf{p}_{\rm tot} = \mathbf{0}$, the center of mass $\mathbf{r}_{\rm c.m.} = \mathbf{0}$, and total angular momentum $\mathbf{L}$ held constant [7]. The formula for the entropy, in addition to the usual δ function energy constraint, has δ function constraints on $\mathbf{p}_{\rm tot}$ and $\mathbf{L}$. We can, for large N, transform this into the canonical ensemble at temperature T, by showing in the usual way that the fluctuations in the energy per particle at constant temperature are $\propto 1\sqrt{N}$ [8].

We wish to calculate the rms size of a chain when $\mathbf{r}_{\text{c.m.}} = \mathbf{0}$: $\langle R^2 \rangle \equiv \frac{1}{N}\langle \sum_{i=1}^{N} r_i^2 \rangle$. For an "ideal" chain [9] with ring topology, the calculation can be done exactly [10] for large N. The δ function constraints are expressed as Fourier integrals by introducing auxiliary variables for integration. The ones associated with $\mathbf{p}_{\text{tot}}$ are trivially handled, whereas the more interesting constraint is $\mathbf{L}$ conservation. This leads to the partition function

$$Z(T, \mathbf{L}) \propto \int e^{i\mathbf{k}\cdot\mathbf{L}} e^{-(T/2)(\mathbf{k}\cdot\mathbf{I}\cdot\mathbf{k}) - \beta U} \delta(\mathbf{r}_{\text{c.m.}}) \prod_{i=1}^{N} d^3\mathbf{r}_i d^3\mathbf{k}, \tag{1}$$

where $\mathbf{I}$ is the moment of inertia tensor of a polymer conformation. Now consider the r integrations. Using spherical symmetry we can choose $\mathbf{k}$ to be along the z direction and these integrals can be turned into functional integrals that look identical to quantum harmonic oscillators but with the zeroth mode ($\mathbf{r}_{\text{c.m.}}$) constrained to zero. Adding a term $\epsilon \sum_i r_i^2$ to βU allows one to differentiate $\ln Z$ with respect to ϵ to obtain $\langle R^2 \rangle$. The results are shown in Fig. 1. The rescaled angular momentum is $L' \equiv L\sqrt{12}/(Nl\sqrt{mk_B T})$, where m is the mass and l is the step length. The probability distribution for L' at temperature T, $P(L')$ is also shown on a log scale. The fact $L' \propto L/N$ can be understood intuitively because a typical value of $L^2/(2I) \sim T$. A typical value of $I \sim (Nm)\langle R^2 \rangle \sim N^2$. Thus the scale for L is $\propto N$.

At $L = 0$, $\langle R^2 \rangle/(Nl^2) = (1 + 15/\pi^2)/36 \approx 0.0700$. Results using a simulation method described below give 0.071 which are the same to within the error bars. This is substantially below, $1/12 \approx 0.083$, the value of the same quantity when conservation of angular momentum is not enforced. When averaged over all angular momenta, the size of the chain must agree with the nonconserved case, and because high L chains will have greatly extended conformations, this must be compensated for by correspondingly compact configurations for small L.

To obtain the asymptotic behavior for large L, using a much simpler argument, we expect that in this limit the dominant configuration of the chain will be a highly stretched circle of radius R rotating symmetrically about the axis of angular momentum. We minimize the free energy, F, of a polymer taking into account both its kinetic energy and elastic energy yielding $R^2/(Nl^2) = L'/(12\pi)$. This also gives $-\beta F = -\pi L'$ The asymptotic slopes for the two graphs in Fig. 1 are precisely these values.

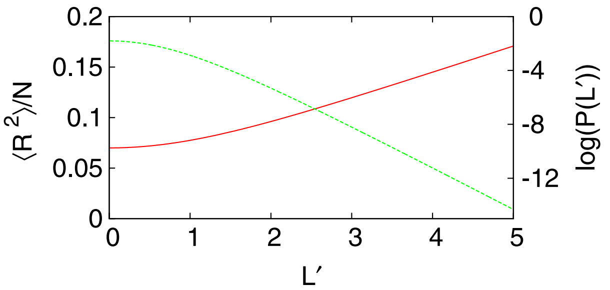

FIG. 1 (color online). The variation of the size of a chain versus its angular momentum for a ideal ring chain (increasing curve). The log of the thermal distribution for different angular momenta (decreasing curve).

The total angular momentum, however, is *not* conserved. Interaction with thermal photons will cause the angular momentum to equilibrate on a time scale that we will now estimate. First we consider the flux of electromagnetic energy emitted by a single polymer. The emission of thermal radiation per unit area of a blackbody is given by the Stephan-Boltzmann law $S = \sigma T^4$, where σ is the Stephan-Boltzmann constant. However, this greatly overestimates the radiation because of the weak efficiency of small objects in emitting light of a far greater wavelength. Calculations for metal nanoparticles (which should be better emitters than dielectric polymers) give a suppression factor of $\approx 2 \times 10^{-3}$ when the nanoparticles are 10 nm in radius [11]. This gives the ratio of $k_B T$ to emitted power $\approx 8 \times 10^{-7}$ s. (More realistically including the effective dielectric of the low density polymer chain will increase this by at least another order of magnitude.) We calculate the relaxation time for self-avoiding chains using the analysis at the end of this Letter. For a 400 amino acid protein which should have a comparable radius of gyration, this gives a relaxation time of $\approx 10^{-9}$ s. Thus in this situation, thermal photon equilibration is more than 2 orders of magnitude slower than the time scale for relaxation of a chain. Therefore, one expects to see transitions in the time averaged radius of gyration of a chain as photons are emitted and absorbed by the polymer. This might be observable in the signature of noise seen in light scattering.

We now turn to a study of the dynamics of these polymers and we see that in this respect, the situation is very different from that of a polymer in a solvent. In both cases, the most basic measure of the dynamics is the monomer-monomer autocorrelation function:

$$g(t) = \left\langle \frac{1}{N} \sum_{i=1}^{N} |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \right\rangle. \tag{2}$$

We will analyze how we expect this to behave and compare it with numerical simulations.

We first consider what kind of coarse grained linear stochastic equation would best approximate the evolution of $\mathbf{r}(s, t)$, the position of the chain at arclength s, and time t. One might first guess that sufficient nonlinearity would introduce strong enough dissipation of individual modes so that the behavior would be similar to that of the Rouse model [12], which describes a "free draining" chain. That is one where individual monomers experience a drag proportional to their velocity $\dot{\mathbf{r}}$. However, there can be no such term as it would violate Galilean invariance, because the center of mass velocity of a chain would then always drift to zero. By symmetry, the lowest order damping term must be $C\partial^3\mathbf{r}/\partial t\partial^2 s$, where C is a constant. Adding in inertia, random forcing $\xi(\mathbf{s},\mathbf{t})$ and chain connectivity gives

$$\frac{\partial^2\mathbf{r}}{\partial t^2} = \left(1 + C\frac{\partial}{\partial t}\right)\frac{\partial^2\mathbf{r}}{\partial s^2} + \xi(\mathbf{s},\mathbf{t}). \tag{3}$$

In terms of each Fourier (or Rouse) eigenmode k along the arclength of the chain, we can solve for the complex frequency $\Omega_k \equiv \omega_k + i\lambda_k$. This gives a damping $\lambda_k \propto k^2$ for small k and $\omega_k \propto k$. This means that for long wavelengths, damping is much smaller than it would be in solution. We write the autocorrelation function $\langle r_k(0)r_k^*(t)\rangle \approx \langle |r_k|^2\rangle \mathrm{Re}[\exp(i\Omega_k t)\Omega_k/\omega_k]$ and because $|r_k|^2$ is approximately $\propto 1/k^2$,

$$g(t) \propto \mathrm{Re}\sum_k \frac{\Omega_k[1-\exp(i\Omega_k t)]}{\omega_k k^2}. \tag{4}$$

For small t, and no dissipation ($\lambda_k = 0$), the behavior of $g(t)$ in the above expression can easily be shown to be $\propto t$, the same law as for a diffusive process. For longer times, the Fourier series shows asymmetric oscillatory behavior, with cusps at minima and parabolic maxima with a period $\propto N$. These same qualitative features will persist for small λ_k so that for large N, these oscillations will slowly damp out with a relaxation time $\propto N^2$.

We now turn to numerical simulations to compare with our expectations. One-dimensional systems are notorious for not being able to equilibrate energy well [13], and even quasi-one-dimensional hard sphere systems [14] exhibit highly nonlocal time correlations, with universal power-law decays [15], which is a general result for one-dimensional chains that are momentum and energy conserving [16].

So we first consider the dynamics of a chain neglecting any self-avoiding interactions, but using an athermal highly nonlinear model for the reasons just mentioned. Thus we have chosen a model where monomers of equal mass are coupled together by links of fixed length, and it is this rigidity that is the source of the nonlinearity. Aside from this constraint, there is no potential energy. The monomers can freely rotate, but there is no coupling to an outside system so that there is no dissipation or random noise term. The model rigorously satisfies conservation of energy, momentum, and angular momentum. An efficient method for evolving such chains was developed so that despite the large number of length constraints, the computation for each time step scales linearly with the number of monomers. The details will be published elsewhere [10]. The angular momentum, center of mass, and energy were monitored to ensure that their drifts due to numerical error remained small for all data used.

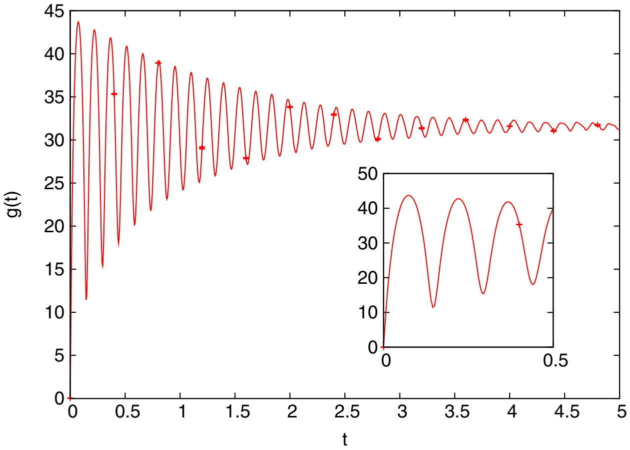

FIG. 2 (color online). The autocorrelation function $g(t)$ as defined in Eq. (2) for a chain of 128 monomers. Double horizontal lines give the very small error bars. The inset shows the beginning of the plot at a higher magnification, where the initial linear increase and cusps are apparent. The time unit is 1,000.

$g(t)$ defined in Eq. (2) was calculated for zero angular momentum chains of different lengths and is displayed in Fig. 2 for $N = 128$ averaged over 24 000 runs. The kinetic energy is set to have an equivalent temperature of 1 and $l = m = 1$. This is very unlike the correlation function for a polymer in solution which shows a smooth slow increase, not the wildly oscillatory form seen here. This is in quite good agreement with the above analysis: the period of oscillations scales as chain length and the short time behavior and cusps are also as one would predict. The form of Eq. (4) was used to fit the numerical data. It is clear from the data that $\omega_k \propto k$, and the damping appears to fit best to a form close to $\lambda_k \propto k^2$. Fitting this to different chain lengths, $N = 64$ and 128, gives a relaxation time $T_{\mathrm{rel}} \propto N^{(1.85\pm.15)}$. Note that in the case of one-dimensional heat conduction, it has been found that even with highly nonlinear models [15], asymptotic large N behavior is difficult to study as more than 10^4 particles must be considered to get a good estimate of critical exponents. Therefore it is possible that the exponent found is off by ~10% of its asymptotic value.

This problem is quite similar to that of a one-dimensional nonlinear chain of particles, which is characterized by long wavelength excitations that slowly decohere and a relaxation time $T_{\mathrm{rel}} \propto N^{3/2}$ [15,16], which is different than the polymer case where we found that the exponent is closer to 2. However, if the polymer chain was stretched by a constant force so that it was quasi-one-dimensional, one would expect the same $N^{3/2}$ scaling for the relaxation time.

A proposal for internal damping, the third order term of Eq. (3), has been made before [17] in connection with Cerf friction [1,18] using a nonrigorous derivation. Adding such a term to the Rouse equation provides an explanation of experiments [6] on extensional relaxation of polymers in solvent. Solvents with different viscosities were considered and extrapolated to the limit of zero viscosity, and the results can be interpreted using such a term. This work lends support to such a mechanism.

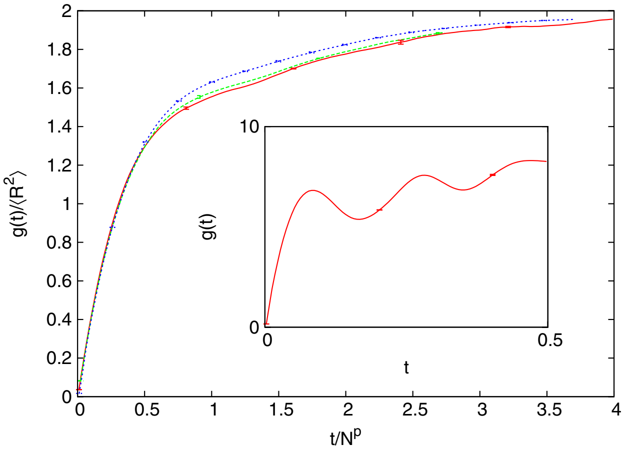

FIG. 3 (color online). The scaled autocorrelation function $g(t)/\langle R^2\rangle$ versus t/N^p, for three chain lengths, $N = 32$, 64, and 128 with short-range repulsive interactions. The inset shows $g(t)$ for an $N = 32$ chain with equal charges at both ends that cause it to stretch. Here $l = 1$.

As one might expect, the inclusion of repulsive interactions between monomers suppresses the oscillations that are seen in the ideal chain. For the sake of efficiency, soft-core potentials were added between monomers having a potential of the form $\beta V(r) = 2[1 - (r/l)^2]^5$. Statistics of such chains with total angular momentum of zero were measured and the size scaling exponent gave $\nu = 0.596 \pm 0.01$ in good agreement with the well-known three-dimensional value.

In Fig. 3 the autocorrelation function for these chains, see Eq. (2), is plotted for chain lengths $N = 32$, 64, and 128, on scaled axes so that they coincide for short times. The vertical axis is $g(t)/\langle R^2\rangle$ and the horizontal one is t/N^p, with p chosen to fit short times best. With $p = 1.15$, the plots coincide well over half of the vertical range, from 0 to 1. However, the long time behavior for $N = 32$ is noticeably above the longer length chains. However, $N = 64$ is only slightly above $N = 128$, and given the correlated error bars, this is barely statistically significant. This is strong evidence that for large N the correlation function approaches the scaling form $g(t) = N^{2\nu} f(t/N^p)$, and therefore the relaxation time for this chain is $\propto N^p$, with $p = 1.15 \pm 0.05$. Note that this is much smaller than that of the ideal chain discussed above, presumably because long range interactions along the chain backbone allow much faster equilibration of energy and momentum. We expect the time it takes a chain segment to move of order its average size R_g should be R_g divided by the center of mass speed for of order half the chain, $\sim N^{-1/2}$, which gives $t_{\mathrm{rel}} \sim N^{1.1}$.

This is in contrast with what happens if charges are added to both ends. With charged protein molecules created during mass spectrometry, a similar situation could also occur. The inset in Fig. 3 shows the autocorrelation function for this case, where the end to end distance is 10.0 ($l = 1$), about one-third of the chain's arclength. The parameters were chosen so that there is still a substantial amount of interaction between neighboring monomers, yet the chain is quite stretched, which is an experimentally realistic scenario. Here one can clearly see oscillations in $g(t)$, intermediate in behavior between the ideal chain and interacting cases.

In conclusion, the equilibrium statistics and dynamics of polymers in a vacuum have many interesting properties. The addition of angular momentum conservation significantly alters chain statistics. The subtle power-law time correlations found in momentum conserving one-dimensional systems can lead to dynamics that are oscillatory and show unusual scaling properties. It is hoped that this work will provide an impetus for further experimental observation of these fascinating systems.

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