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Exact solution to ideal chain with fixed angular momentum

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The statistical mechanics of a noninteracting polymer chain in the limit of a large number of monomers is considered when the total angular momentum **L** is fixed. The radius of gyration for a ring polymer in this situation is derived exactly in closed form by functional integration techniques. Even when $L=0$ the radius of gyration differs from that of a random walk by a prefactor of order unity. The dependence on L is discussed qualitatively and the large-L limit can be understood by physical arguments, which can also be extended to self-avoiding chains.

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I. INTRODUCTION

The statistical properties of polymers have been the subject of intensive research for many decades [1]. However, these efforts have been almost entirely confined to polymers in liquids or solids, while in contrast their properties in a vacuum have received little attention. Until recently there were not clear physical realizations of such situations, but recent developments have changed this as will now be discussed briefly. Mass spectrometry techniques have been developed using lasers that desorb whole proteins into a vacuum where their mass can be determined by measuring the time of flight [2]. It might be possible to probe molecules such as DNA using optical tweezers in a manner similar to what is done routinely in solution [3], and use this to probe in detail the polymer's dynamics. In such a case, there may prove to be applications in determining the structure of biomolecular complexes. For example, DNA often has molecules bound to it, such as regulatory proteins, that are not easily observable. Probing DNA in a vacuum might prove to be more efficacious than in a solution because of the importance of inertial effects that we will see play a much more important role than in a solvent. Finally, in the search for long hydrocarbon molecules in interstellar media [4], such systems are now of experimental interest. Short chains in this situation have been modeled [4] in order to compare experimental spectroscopic frequency data with theory in order to determine the chain's structure. It is therefore useful to extend this to model longer chains, for the same purpose.

The author [5] recently considered such systems theoretically and by means of computer simulation, and the purpose of this paper is to present an exact derivation for the radius of gyration of a polymer in a vacuum with conserved angular momentum. The solution requires periodic boundary conditions for the chain, which means we are considering a ring polymer (ring DNA being a potential experimental example). The qualitative features found persist for linear chains as well, as has been confirmed by computer simulations [5].

In reality, angular momentum conservation is weakly broken by interaction with thermal electromagnetic radiation [5] but it is still important to understand the case of conservation laws properly in order to understand these more complicated effects. Also intrachain interactions are not considered; in other words, this is the case of an "ideal" chain [1]. In standard treatments of statistical mechanics, angular momentum conservation is mostly ignored as it is thought to have no effect on the results obtained, for a large number of degrees of freedom. Therefore what we will find is at first sight rather surprising, that a polymer chain with conserved total energy E, total linear momentum $\mathbf{p}_{\rm tot}=\mathbf{0}$, and total angular momentum **L** has a radius of gyration that depends strongly on L, so that even when $L=0$ the radius of gyration differs significantly from that of an ideal chain without this restriction. The somewhat counterintuitive nature of this effect makes it worthwhile to prove it for an exactly solvable model, which is the main point of this work.

We will show in Sec. II that the microcanonical formulation of this problem, with all conservation laws enforced, can be expressed in a canonical ensemble in the limit of large N, after which it can be converted to a functional integral. This can then be evaluated to obtain the radius of gyration as a function of angular momentum **L**. We will analyze in Sec. II A how this can be understood more physically in the limit of large total angular momentum, and use this method to derive the scaling behavior of a ring with excluded volume interactions. In Sec. II B, we analyze the relation between the temperature and total energy. In Sec. II C we calculate the distribution of angular momentum in equilibrium. In the derivation, we used a quadratic potential between neighboring monomers. In Sec. II D we show how the results found should be universally true for a large class of models with nonquadratic potentials. Finally, in Sec. III, we conclude with a discussion of the importance of ergodicity in the dynamics and a brief comparison with numerical results.

II. DERIVATION OF MAIN RESULTS

The statistical mechanics of a classical system of N particles interacting via a general potential Φ, and with conserved total energy, momentum, and angular momentum, has been considered previously by Laliena [6]. He has shown that the conservation of linear momentum does not affect answers obtained in the microcanonical ensemble with conservation of angular momentum enforced [7]. So we will write down the volume of phase space with **L** and energy E kept constant,

$$W(E,L,N)=C\int \delta(E-K-\Phi)\,\delta^{(3)}\Big(\mathbf{L}-\sum_i \mathbf{r}_i\times\mathbf{p}_i\Big)\times\delta^{(3)}(\mathbf{r}_{\rm c.m.})\left(\prod_{i=1}^{N} d^3r_i d^3p_i\right) \quad (1)$$

where the coordinates are $\{\mathbf{r}_i\}$ and momenta are $\{\mathbf{p}_i\}$. C is a constant that involves N and $\hbar$ and is of no consequence for the purposes here. K is the kinetic energy $\Sigma_i p_i^2/2m$, with m the mass of each monomer, and here we are taking them all to be equal. The center of mass $\mathbf{r}_{\text{c.m.}}$ also must be conserved and is set to 0. We use the Fourier representation of the δ functions to write this as

$$W(E,L,N) \propto \int_C d\lambda\, e^{\lambda E} \int e^{-\lambda(K+\Phi)} \delta^{(3)}\left(\mathbf{L} - \sum_i \mathbf{r}_i \times \mathbf{p}_i\right) \times \delta^{(3)}(\mathbf{r}_{\text{c.m.}}) \left(\prod_{i=1}^{N} d^3 r_i d^3 p_i \right). \tag{2}$$

As shown by Lax [8], for most purposes, as discussed below, the contour of integration can be deformed in the complex λ plane using the method of steepest descents. The three conditions are (a) that a saddle point exists, (b) that an observable not be of order $\exp(\text{const} \times N)$, and (c) that there be no singularity in the observable in the neighborhood of the saddle point. Conditions (b) and (c) are first obtained through the canonical ensemble and then tested to see if they are satisfied. Condition (a), that a saddle point exists, is satisfied because we can find a relationship between the energy and the temperature. In the case of an athermal system, say of rigid links, this would just be that $E \propto 1/\beta$, where β is the value of λ at the saddle point. Condition (b) is satisfied for the quantity of interest here, the average radius of gyration. Condition (c) is also satisfied because we will see that the average radius of gyration is a smooth function of the temperature for finite $T = 1/\beta$. Thus we can drop the integration over λ and replace λ by the inverse temperature β, and consider the partition function Z instead of the phase space volume integral (which is simply related to the entropy):

$$Z(\beta,L,N) \propto \int d^3k \int e^{i\mathbf{k}\cdot\mathbf{L}} e^{-\beta(K+\Phi)} \exp\left(-i\mathbf{k}\cdot \sum_i \mathbf{r}_i \times \mathbf{p}_i\right) \times \delta^{(3)}(\mathbf{r}_{\text{c.m.}}) \left(\prod_{i=1}^{N} d^3 r_i d^3 p_i \right). \tag{3}$$

Integrating over the $\mathbf{p}_i$'s we obtain

$$Z(\beta,L,N) \propto \int d^3k\, e^{i\mathbf{k}\cdot\mathbf{L}} \int e^{-1/2\beta \mathbf{k}\cdot I \cdot \mathbf{k}} e^{-\beta\Phi} \prod_{i=1}^{N} d^3 r_i \equiv \int d^3k\, e^{i\mathbf{k}\cdot\mathbf{L}} \zeta(\beta,\mathbf{k}). \tag{4}$$

Here I is the moment of inertia tensor for the particles,

$$I_{\alpha\gamma} = m \sum_{i=1}^{N} (r_i^\nu r_i^\upsilon \delta^{\alpha\gamma} - r_i^\alpha r_i^\gamma), \tag{5}$$

where α and γ label the coordinates (1,2,3), and the Einstein summation convention has been used for ν. In the last equality of Eq. (4) we have introduced the function $\zeta(\beta,\mathbf{k})$. Note that this cannot depend on the direction of $\mathbf{k}$ but only on its magnitude, if Φ involves only isotropic central potentials. Therefore we can take $\mathbf{k}$ to be along the z axis, $\mathbf{k} = k\hat{z}$, and write

$$\zeta(\beta,k) = \int \exp\left(-mk^2/2\beta \sum_i (x_i^2 + y_i^2) - \beta\Phi\right) \times \delta^{(3)}(\mathbf{r}_{\text{c.m.}}) \prod_{i=1}^{N} d^3 r_i. \tag{6}$$

Because the dependence of ζ on $\mathbf{k}$ is only radial, we can also perform the $\mathbf{k}$ angular integrals in Eq. (4), rewriting the $\mathbf{k}$ integration in spherical coordinates and obtaining

$$Z(\beta,L,N) = \frac{c}{L} \int_0^\infty k \sin(kL) \zeta(\beta,k) dk \tag{7}$$

where c is a constant that plays no role in the subsequent analysis.

It should be noted that, although the above derivation now involves no explicit energy conservation, this is still mathematically equivalent, in the limit of large N, to the initial formulation at fixed energy, momentum, and angular momentum. We will return to this point later in Sec. II B, when we discuss the dependence of temperature on the angular momentum, and in the discussion, Sec. III.

The potential is taken to be that of an ideal Gaussian chain with step length l and a ring topology,

$$\beta\Phi_0 = \frac{3}{2l^2} \left(\sum_{i=1}^{N-1} |\mathbf{r}_{i+1} - \mathbf{r}_i|^2 + |\mathbf{r}_N - \mathbf{r}_1|^2 \right). \tag{8}$$

We expect by the central limit theorem that many models of polymer chains will all give the same results for most quantities of interest, if the overall radius of gyration is $\ll N$. We will establish this in more detail in Sec. II D.

In order to calculate the radius of gyration, one can add an additional potential with a parameter ϵ,

$$\beta\Phi = \beta\Phi_0 + \epsilon l \sum_{i=1}^{N} |\mathbf{r}_i|^2, \tag{9}$$

so that the average radius of gyration can be written as

$$R_g^2 = \left\langle \frac{1}{N} \sum_{i=1}^{N} |\mathbf{r}_i|^2 \right\rangle = -\frac{1}{Nl} \frac{\partial \ln Z}{\partial \epsilon} \bigg|_{\epsilon=0}. \tag{10}$$

The integration in Eq. (6) is Gaussian and we can now take the usual limit to turn this into a functional integral,

$$\zeta(\beta,k) = \int \exp\left\{ -\int_0^M \left(\frac{Tmk^2}{2l} + \epsilon \right) \left[x^2(s) + y^2(s) + \epsilon z^2 + \frac{3}{2l} |\dot{\mathbf{r}}|^2 ds \right] \right\} \delta^{(3)}(\mathbf{r}_{\text{c.m.}}) \delta\mathbf{r}(s). \tag{11}$$

The functional integrations in the x, y, and z directions decouple and the x and y functional integrals are identical. Each one of these three integrals is of the form of the partition function of a one-dimensional quantum harmonic oscillator at finite temperature except for the restriction on the center of mass. If we consider the Euclidean time action for a quantum harmonic oscillator of mass M at inverse temperature β_0,

$$S = \int_0^{\beta_0} \frac{M}{2}(\dot{x}^2 + \omega_0^2 x^2)dt, \tag{12}$$

then the partition function

$$Z_0 = \int e^{-S}\delta x(t) \propto \frac{1}{2\,\sinh(\beta_0\omega_0/2)} \tag{13}$$

with periodic boundary conditions on the paths $x(0)=x(\beta_0)$. This is true because of the general formula relating the partition function to the Euclidean path integral over times ranging from 0 to the inverse temperature [9]. The partition function Eq. (13) can also be derived in a less elegant but more direct manner by writing all paths in terms of a Fourier expansion, which then decouples the integrals, and forms an infinite product over all modes. This latter approach is useful in the present application because we have the additional restriction on the path integral that the zero mode should not be integrated over as a consequence of the restriction on the center of mass. Using the Fourier decomposition approach, we can easily incorporate this restriction, by not including the zero mode in the product. This amounts to multiplying Eq. (13) by ω_0

Rescaling variables so that the angular momentum $L' \equiv L\sqrt{12}/(Nl\sqrt{mT})$ and using Eq. (10) gives

$$\frac{R_g^2}{Nl^2} = \frac{1}{36}\frac{\displaystyle\int_0^\infty (k[-6+k^2+6k\,\coth(k)]\text{csch}(k)^2\sin(kL'))dk}{\displaystyle\int_0^\infty k^3\,\text{csch}(k)^2\sin(kL')dk}. \tag{14}$$

Both the numerator and denominator can be computed in closed form using contour integration. This gives the final result

$$\frac{R_g^2}{Nl^2} = \frac{2L'(3+\pi^2) + L'(\pi^2-6)\cosh(L'\pi) + 3(L'^2-1)\pi\,\sinh(L'\pi)}{36\pi[2L'\pi + L'\pi\,\cosh(L'\pi) - 3\,\sinh(L'\pi)]}. \tag{15}$$

A plot of this equation is displayed in Fig. 1.

For $L'=0$ this reduces to $R_g^2/(Nl^2)=(1+15/\pi^2)/36 \approx 0.07$. For a ring without angular momentum conservation, $R_g^2/(Nl^2)=(1/12)\approx 0.083$, which means that the restriction to $L=0$ causes the rings to be smaller relative to the case where the angular momentum can take on any value.

A. Large-*L* limit

1. Ideal chains

In the opposite limit of large L', $R_g^2/(Nl^2)\to L'/(12\pi)$. Note that in terms of L, $R_g^2 \to Ll/(\pi\sqrt{12Tm})$ independent of chain length N. To understand this behavior, we consider high-L configurations, where we expect that a typical configuration of the ring will be close to a circle rotating rapidly. The approximate free energy contains a kinetic energy and an elastic term

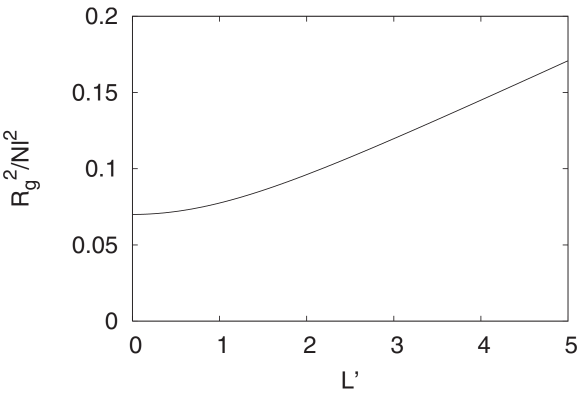

FIG. 1. Radius of gyration versus rescaled angular momentum for an ideal ring chain.

$$F = \frac{L^2}{2I} + \frac{k}{2}C^2, \tag{16}$$

where $C=2\pi R$ is the circumference, and k is the entropic elastic spring coefficient $k=3T/(Nl^2)$. The moment of inertia is approximately $I=mNR^2$. Minimizing F with respect to R^2 gives the above result. It is not surprising that this result is exact because in the large-L limit we expect that this circular configuration will become dominant.

2. Excluded volume interactions for large L

The fact that in this limit we obtain the exact asymptotic dependence for R_g on L suggests that this can be extended to chains with excluded volume satisfying $R_g \sim N^\nu$, with $\nu \approx 3/5$ in three dimensions. In this case the elastic free energy is known [1] up to a prefactor from the entropy

$$S \sim \left(\frac{R}{N^\nu}\right)^{1/1-\nu}, \tag{17}$$

and using this in the equation for the free energy, Eq. (16), and then minimizing with respect to R gives

$$R \sim L^{2(1-\nu)/3-2\nu} N^{2\nu-1/3-2\nu}. \tag{18}$$

B. Lack of dependence of *T* on *L*

The temperature in this model at a given energy is determined in the usual way, by requiring that the average energy in the canonical ensemble is equal to the microcanonical energy. However, in this case, the radius of gyration is a very sensitive function of L. To see this, note that changes occur on a scale $L' \sim 1$, or $L \sim Nl\sqrt{mT}$. Because I is typically $\sim (Nm)R_g^2 \sim (Nm)(Nl^2) \sim N^2 l^2 m$ then $L \sim Nl\sqrt{mT}$. The order of $L^2/2I$ is therefore $\sim T$. This means that a change of order one degree of freedom changes $R_g^2/(Nl^2)$ by a number of order unity, which has a negligible effect on the temperature but a large effect on the radius of gyration. So for fixed L', as $N \to \infty$, we see that in the canonical ensemble, the effect of the angular momentum constraint on the energy is a fraction of order $1/N$. This means that when the limit $N \to \infty$ is taken with L' fixed, the relation between the temperature and energy can be obtained as it would be for a polymer without angular momentum conservation, and thus will not have any dependence on L'. This is also seen more rigorously by computing the exact dependence of the partition function on L', which is done below in Sec. II C.

C. Thermal distribution of *L*

It is useful to calculate the probability density for finding the polymer with a particular value of total (rescaled) angular momentum L'. This should be important in the case where there is a dilute gas of such polymers. It is also important for a single chain for long times, since the angular momentum is changed by the weak coupling to electromagnetic blackbody radiation [5]. In this case the probability density function $P(L')$ is proportional to the partition function $Z(\beta, L', N)$. The normalization requirement is that

$$\int_0^\infty P(L') 4\pi L'^2 dL' = 1. \tag{19}$$

The normalization is straightforward to calculate using Eq. (7) and integrating over L' first. The L' integration requires evaluating

$$\int_0^\infty L' \sin(kL') dL' = -\int_0^\infty \frac{d\cos(kL')}{dk} dL' = -\pi\delta'(k), \tag{20}$$

and, using this, the integral over k is now easily accomplished:

$$\int_0^\infty Z(\beta, L', N) 4\pi L'^2 dL = c\pi \left. \frac{\partial(k\zeta(\beta,k))}{\partial k} \right|_{k=0}. \tag{21}$$

Z was evaluated previously in the process of calculating the radius of gyration and is proportional to

$$\int_0^\infty k^3 \operatorname{csch}(k)^2 \sin(kL') dk / L'. \tag{22}$$

Evaluating this integral and including the correct normalization using Eq. (21) yields

$$P(L') = \frac{\pi^3 \operatorname{csch}(L'\pi/2)^4 [2L'\pi + L'\pi \cosh(L'\pi) - 3\sinh(L'\pi)]}{16 L' \pi^2}. \tag{23}$$

$\ln[P(L')]$ versus L' is plotted in Fig. 2. Because of the nonconstant value of the moment of inertia for the chain, this distribution is decidedly non-Gaussian. In the large-L' limit, the slope of this curve approaches a constant with a slope of $-\pi$. This is in agreement with the minimization argument for large L' given under Eq. (16).

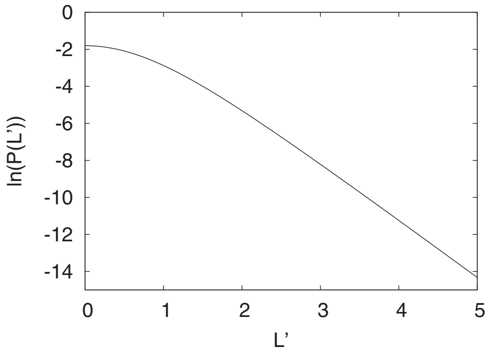

FIG. 2. Probability density function for finding a chain in thermal equilibrium with rescaled angular momentum L' for an ideal ring chain.

D. Universality of results for ideal chains

We now return to a more detailed analysis of the question of the universality of these results. In particular, the exact results were derived for a Gaussian ideal chain. In general, the links coupling monomers together will not be quadratic but some more general functional form $V(\Delta)$ that can be expanded in a power series in Δ. We know that, without the constraint of angular momentum conservation, the large-distance properties, such as the radius of gyration, are well described by a Gaussian ideal chain. However, we should analyze whether this continues to be the case with the additional constraints imposed here. Consider a continuous chain $\mathbf{r}(s)$. We can ask what happens if we add higher-order terms in the expansion of the potential:

$$\Phi_0 = \frac{3}{2l} \int_0^{Nl} \left(\left| \frac{d\mathbf{r}}{ds} \right|^2 + \sum_{n=3}^{\infty} a_n \left| \frac{d\mathbf{r}}{ds} \right|^n \right) ds, \tag{24}$$

where a_n are determined by the coefficients of the expansion of V. Rescaling variables so that $s' = s/(Nl)$ and $\rho = \mathbf{r}/\sqrt{Nl^2}$,

$$\Phi_0 = \frac{3}{2}\int_0^1 \left(\left| \frac{d\rho}{ds'} \right|^2 + \sum_{n=3}^{\infty} a_n N^{1-n/2} \left| \frac{d\rho}{ds'} \right|^n \right) ds' . \quad (25)$$

In Eq. (11) of the above analysis, we can generalize Φ_0 to include these a_n's and then can take the limit $N \to \infty$ but with Nl^2 held constant and with rescaled angular momentum $L' \propto Ll$ held constant. Then all the above terms in the summation go to zero and we recover the Gaussian form for Φ_0 that we used in the derivation. Therefore we expect the results Eqs. (15) and (23) to hold for a wide variety of local couplings between monomers. This was confirmed by computer simulations, as discussed below.

As usual with such arguments, the value of the Kuhn step length l has not been determined. This argument only shows that such a step length exists. The actual value of it will depend on the detailed molecular structure, as is the case for polymers in solution [1].

III. DISCUSSION

It is of interest to compare the extreme sensitivity of a polymer to restrictions in angular momentum with what would be expected for other kinds of systems. The system considered here is essentially one dimensional in that interactions are only from nearest neighbor monomers. In, for example, a membrane or a three-dimensional gel, the system is of higher dimension. In such two- or three-dimensional systems, a perturbation that changes the free energy by $O(k_BT)$ is expected to affect averages by only microscopic amounts. However, for polymers, it has a much larger effect. For example, a force pulling the ends of a polymer costing k_BT of energy will increase its radius of gyration by a multiplicative constant of order unity. Because a polymer chain with the restriction $L=0$ reduces the number of degrees of freedom by at least one, it should affect the free energy by $O(k_BT)$. So, by the above argument, this is expected to make nontrivial changes to its statistics, unlike in higher-dimensional systems. So even for the case $L=0$ the noninteracting polymer is no longer described correctly as an uncorrelated random walk.

Where this derivation will fail is in cases where the system cannot be adequately described by the microcanonical ensemble, or equivalently, when the system is not ergodic. For sufficiently nonlinear interactions between neighboring monomers and large N, ergodicity is expected to occur for most three-dimensional systems, and experimentally all systems appear to be ergodic enough to obey statistical mechanics. However, for one-dimensional chains with nonlinear interactions, such as studied by Fermi, Pasta, and Ulam [10], such equilibration can be quite slow and depends in detail on the initial modes that have been excited [11]. Computer simulations for polymer molecules have recently been performed to look at Lyapunov exponents, and these can be very small for systems close to a phase transition, such as the coil-globule transition [12]. More strongly nonlinear athermal models such as the Sinai-Chernov pen case model [13] and the random collision model [14], do not suffer from these equilibration effects. Therefore, to investigate the equilibrium properties discussed in this work, simulations of a highly nonlinear athermal polymer model have been recently undertaken [5]. The model used was one of rigid links with a fixed distance between monomers. The links could rotate freely aside from this constraint. The simulation obeyed conservation of energy, momentum, and angular momentum to high precision. It gave the same radius of gyration for $L=0$ as predicted by this theoretical analysis, confirming the validity of the ergodic hypothesis for this case, and the subsequent theoretical analysis of Sec. II. In this case $R_g^2/(Nl^2)$ was found to be 0.071, which is the same as the exact result mentioned above, ≈ 0.07, to within statistical error.

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