

Exact Solution to Ideal Chain with Fixed Angular Momentum

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Abstract

The statistical mechanics of a non-interacting polymer chain in the limit of a large number of monomers is considered when the total angular momentum, \mathbf{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.

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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 now with recent developments in the mass spectrometry of proteins [2] and the search for long hydrocarbon molecules in interstellar media [3], such systems are now of experimental interest. The author [4] 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.

In reality angular momentum is weakly broken by interaction with thermal electromagnetic radiation [4] but it is still important to understand the case of conservation laws properly in order to understand these more complicated effects. Also intra-chain interactions are not considered, that is this is the case of an “ideal” chain [1]. What we will find is at first sight rather surprising, that a polymer chain with conserved total energy E , total linear momentum $\mathbf{p}_{tot} = 0$, and total momentum \mathbf{L} , has a radius of gyration that depends strongly on L , so even when $L = 0$, the radius of gyration differs significantly from that of an ideal chain without this restriction.

The statistical mechanics of a general classical system of N particles with constant total energy, momentum, and angular momentum with coordinates $\{\mathbf{r}_i\}$ and momenta $\{\mathbf{p}_i\}$ has been considered previously by Laliena [5]. They were considered to be interacting via a general potential Φ . In the case under consideration here, this microcanonical formulation 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 \mathbf{L} .

Laliena [5] has shown that the conservation of linear momentum does not effect answers obtained in the microcanonical ensemble with conservation of angular momentum enforced [6]. So we will write down the volume of phase space with \mathbf{L} and energy E kept constant.

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

C is a constant here that involves N and \hbar and is of no consequence for the purposes here. K is the kinetic energy $\sum_i p_i^2/2m$, with m the mass of each monomer, and here we are

taking them all to be equal. The center of mass \mathbf{r}_{cm} also must be conserved and is set to 0. We use the Fourier representation of the δ functions to write this as

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

As shown by Lax [7], 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, (a) that a saddle point exists, (b) that an observable not be of order $\exp(const.N)$, 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 smooth function of the temperature for T 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 instead of the phase space volume integral (which is simply related to the entropy.)

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

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

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

where I is the moment of inertia tensor for the particles

$$I_{\alpha\gamma} = m \sum_{i=1}^N (r_i^\nu r_i^\nu \delta_{\alpha\gamma} - r_i^\alpha r_i^\gamma) \quad (5)$$

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 its magnitude, if Φ only involves isotropic central potentials. Therefore we can take \mathbf{k} to be along the z axis: $\mathbf{k} = k\hat{z}$, and write

$$\zeta(\beta, k) = \int e^{-\frac{mk^2}{2\beta} \sum_i (x_i^2 + y_i^2) - \beta\Phi} \delta^{(3)}(\mathbf{r}_{cm}) \prod_{i=1}^N d^3 r_i \quad (6)$$

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

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

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

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

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

By the central limit theorem, many models of polymer chains will all give the same results for most quantities of interest, if the overall radius of gyration is $\ll N$.

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

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

so that the average radius of gyration can be written as

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

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

$$\zeta(\beta, k) = \int e^{-\int_0^{Nl} \left(\frac{Tmk^2}{2l} + \epsilon \right) (x^2(s) + y^2(s)) + \epsilon z^2 + \frac{3}{2l} |\dot{\mathbf{r}}|^2 ds} \delta^{(3)}(\mathbf{r}_{cm}) \delta \mathbf{r}(s) \quad (11)$$

The functional integration 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 oscillators at finite temperature except for the restriction on the center of mass. If we consider the Euclidean time action for a quantum harmonic oscillators of mass M at inverse temperature β_o

$$S = \int_0^{\beta_o} \frac{M}{2} (\dot{x}^2 + \omega_0^2 x^2) dt \quad (12)$$

then the partition function

$$Z_o = \int e^{-S} \delta x(t) \propto \frac{1}{2 \sinh\left(\frac{\beta_o \omega_0}{2}\right)} \quad (13)$$

with periodic boundary conditions on the paths $x(0) = x(\beta_o)$. 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 [8]. 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

$$\frac{R_g^2}{Nl^2} = \frac{1}{36} \frac{\int_0^\infty (k(-6 + k^2 + 6k\coth(k))\operatorname{csch}(k)^2 \sin(kL'))dk}{\int_0^\infty k^3 \operatorname{csch}(k)^2 \sin(kL')dk} \quad (14)$$

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

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

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.

In the opposite limit of large L' , $R_g^2/(Nl^2) \rightarrow L'/12\pi$. Note that in terms of L , $R_g^2 \rightarrow Ll/(\pi\sqrt{12Tm})$ 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

$$F = \frac{L^2}{2I} + \frac{k}{2}C^2 \quad (16)$$

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 with respect to R^2 this 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.

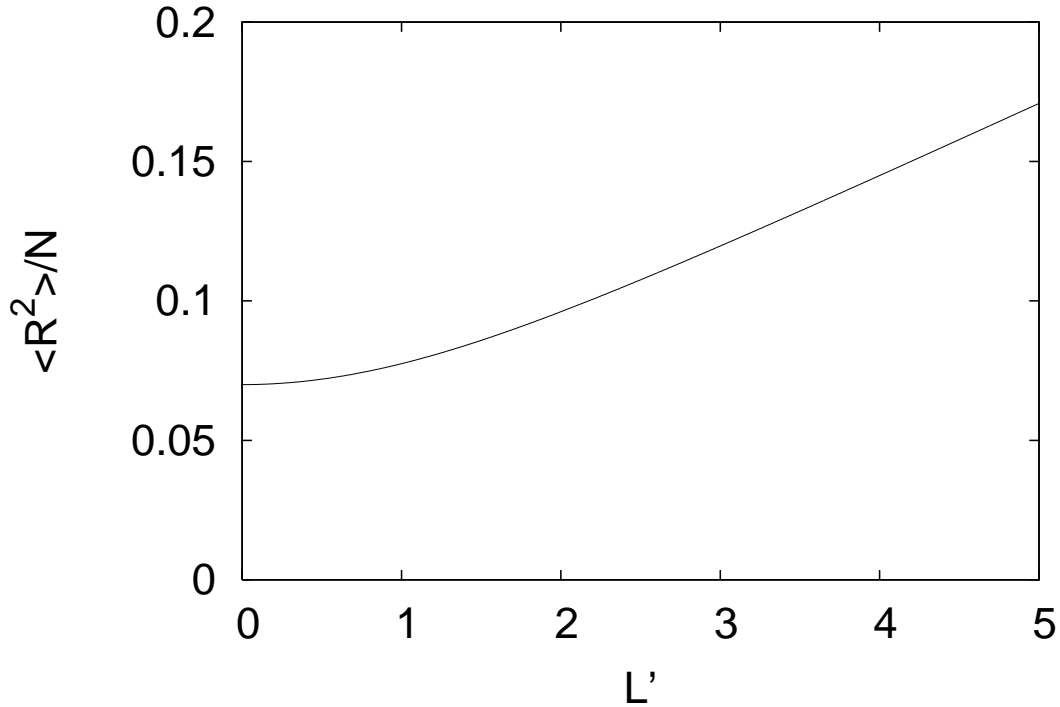


FIG. 1: The radius of gyration versus rescaled angular momentum for an ideal ring chain.

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 $\sim (Nm)R_g^2 \sim (Nm)(Nl^2) \sim N^2l^2m$ 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 $N \rightarrow \infty$, 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 $N \rightarrow \infty$ is taken with L' fixed, the relation between the temperature and energy can be obtained as it would 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.

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 black body radiation [4]. In this case the probability density function $P(L')$ is proportional to the partition function $Z(\beta, L', N)$. The normalization requirement is that

$$\int_0^\infty P(L') 4\pi L'^2 dL' = 1 \quad (17)$$

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

$$\int_0^\infty L' \sin(kL') dL' = - \int_0^\infty \frac{d \cos(kL')}{dk} dL' = -\pi \delta'(k) \quad (18)$$

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

$$\int_0^\infty Z(\beta, L', N) 4\pi L'^2 dL' = c\pi \frac{\partial(k\zeta(\beta, k))}{\partial k} \Big|_{k=0} \quad (19)$$

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

$$\int_0^\infty k^3 \operatorname{csch}(k)^2 \sin(kL') dk / L' \quad (20)$$

Evaluating this integral and including the correct normalization using Eq. 19 yields

$$P(L') = \frac{\pi^3 \operatorname{csch}(\frac{L'\pi}{2})^4 (2L'\pi + L'\pi \cosh(L'\pi) - 3 \sinh(L'\pi))}{16L'\pi^2} \quad (21)$$

$\ln(P(L'))$ versus L' is plotted in Fig. 2. Because of the non-constant 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.

It is interesting to compare the extreme sensitivity of this system to restrictions in angular momentum, with what would be expected in 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 $\mathcal{O}(k_B T)$ is expected to only effect averages by microscopic amounts. However for polymers, it has a much larger effect. For example, a force pulling the ends of a polymer

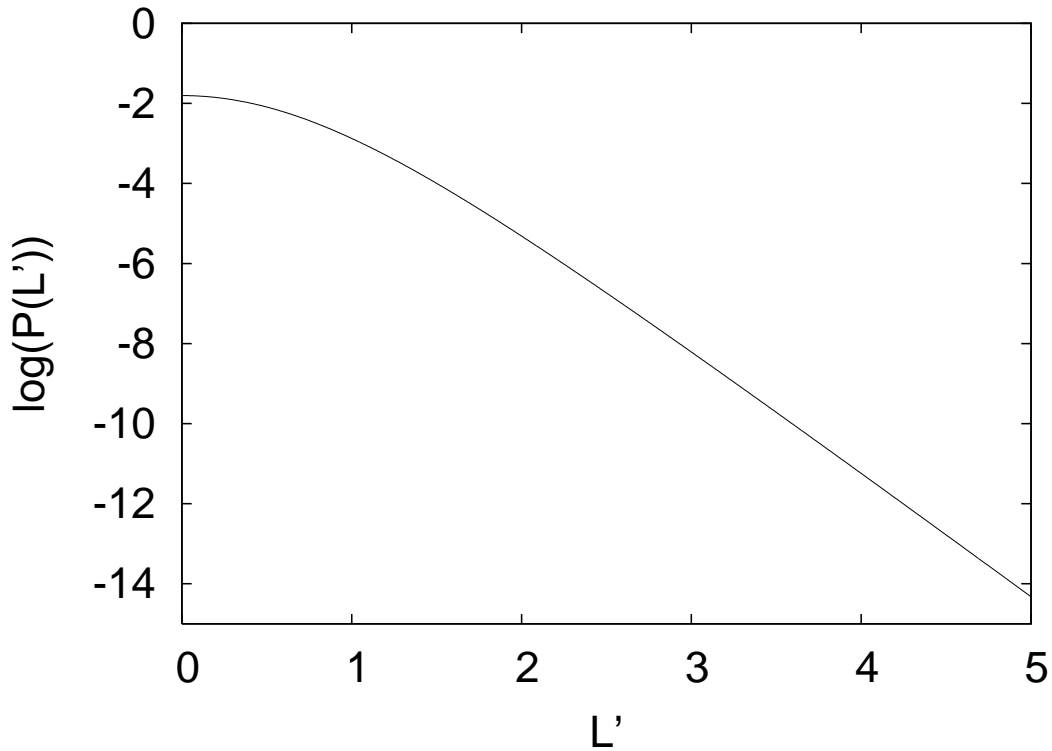


FIG. 2: The probability density function for finding a chain in thermal equilibrium with rescaled angular momentum L' for an ideal ring chain.

costing $k_B T$ 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 $\mathcal{O}(k_B T)$. So by the above argument, this is expected to make non-trivial changes to its statistics, unlike higher dimensional systems. So even in the case $L = 0$, the non-interacting polymer is no longer an uncorrelated random walks.

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