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LETTER TO THE EDITOR

Unusual bifurcation in a constrained random walk system

Jens Rieger

Theoretische Physik, Universität des Saarlandes, 6600 Saarbrücken, Federal Republic of Germany

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Abstract. A random walk with fixed arc length and fixed endpoints which has to pass through k fixed points is considered. It is shown analytically that for the case $k=1$ and equal distance R between the respective endpoints and the intermediate point a bifurcation occurs with respect to the arc length which the walk traces out between its origin and the intermediate point if R falls below a critical value. From numerical results it follows that this bifurcation also occurs in the following cases: when the intermediate point is not equidistantly positioned between the endpoints; when the walk is not confined to a point but to a hoop; and when the walk has to pass through several points ($k>1$).

The model we discuss in this letter may be defined in its most general form as follows: a RW (or idealised polymer chain) consisting of N steps of length b is embedded in $\mathbb{R}^d$ where $d \geqslant 2$. It starts at $\boldsymbol{R}_0 = \boldsymbol{0}$, has to pass through k points $\boldsymbol{R}_i$ and ends at $\boldsymbol{R}_{k+1}$. This model is termed the slip-link model in the polymer literature [1–5] for the polymer chain is forced to pass through imaginary hoops (the links) of negligible diameter located at $\{\boldsymbol{R}_i\}$ and is furthermore allowed to fluctuate (slip) through the hoops. We seek in the following the statistics of the respective arc lengths $\{l_i\}$ displayed by the chain between any pair of points $\{\boldsymbol{R}_{i-1}, \boldsymbol{R}_i\}$, $i = 1, 2, \ldots, k+1$, which are visited in a consecutive manner. As will be shown these statistics differ under certain conditions from what might be expected intuitively, i.e. the equipartitioned state $l_i = Nb/(k+1)$ is not always the most probable one. The present model system has already been very briefly outlined in [6].

Casting the problem into the conventional continuous walk representation [7] the normalised probability density function (PDF) for a specific configuration $\{l_1, l_2, \ldots, l_{k+1}\}$ subject to the condition $\Sigma l_i = Nb \equiv L$ with the points $\boldsymbol{R}_i$ being fixed is given by the following (formal) functional integral:

$$P_k(\{\boldsymbol{R}_i\}; \{l_i\}) = \mathcal{N}^{-1} \int_{\boldsymbol{r}(0)=\boldsymbol{R}_0}^{\boldsymbol{r}(L)=\boldsymbol{R}_{k+1}} \mathcal{D}[\boldsymbol{r}(\tau)] \prod_{i=1}^{k+1} \delta(\boldsymbol{r}(\tau_i) - \boldsymbol{R}_i) \exp\left[-\frac{d}{2b} \int_{\tau_{i-1}}^{\tau_i} \left(\frac{\mathrm{d}\boldsymbol{r}(\tau)}{\mathrm{d}\tau} \right)^2 \mathrm{d}\tau \right] \tag{1}$$

where $\tau_i = \Sigma_{j=0}^{i} l_j$ and $l_0 = 0$. The normalisation constant $\mathcal{N}$ is obtained by integrating the integral in (1) over all possible configurations $\{l_i\}$.

First, we consider the case $k=1$ and $|\boldsymbol{R}_1| = |\boldsymbol{R}_2 - \boldsymbol{R}_1| = R$. Using a known result for the unconstrained RW (see e.g. [7]) $P_1(\{\boldsymbol{R}_i\}, \{l_i\})$ can be given by the following conditional probability:

$$P_1(\{\boldsymbol{R}_i\}, \{l_i\}) \sim [l(L-2)]^{-d/2} \exp\left(-\frac{d}{2} \frac{R^2 L}{b} \frac{1}{l(L-l)} \right) \tag{2}$$

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where $l \equiv l_1$ and $l_2 = (L - l)$. The extrema of $P_1(\{\boldsymbol{R}_i\}; \{l_i\})$ are computed by differentiation of (2) with respect to l. One finds easily that $P_1(\{\boldsymbol{R}_i\}; \{l_i\})$ exhibits one maximum or two maxima (separated by a minimum) depending on the value of R for the following values of l:

$$l_{\text{ext}} = \begin{cases} L/2 & \text{if } R > R_c \equiv (Lb/4)^{1/2} \\ L/2 \pm (L^2/4 - LR^2/b)^{1/2} & \text{if } R < R_c. \end{cases} \tag{3}$$

When considering the R dependence of l_{ext} [6] one obtains a figure which is strongly reminiscent of the temperature dependence of the order parameter M in a system exhibiting a second-order phase transition if we identify R_c^2 with T_c and $[l_{\text{ext}} - L/2]$ with M. This analogy can be further pursued by consideration of the free energy $F = -kT \ln[P_1(\{\boldsymbol{R}_i\}; \{l_i\})]$ of the RW system which is computed via the Boltzmann entropy. $F(l)$ is plotted in figure 1 for several values of R. The dependence of $F(l)$ on $l - L/2$ is again akin to the order parameter dependence of the free energy of a system with a finite number of degrees of freedom which undergoes a second-order phase transition in the thermodynamic limit [8]. But in contrary to a system exhibiting a phase transition where the height of the free energy barrier between the two branches of the bifurcation tends to infinity in the limit of infinite system size we find that in the present case the height of the free energy barrier $\Delta F = F(L/2) - F(l_{\text{ext}})$ is for all $R > 0$ and all N of the order of kT (cf also figure 1):

$$\Delta F = \tfrac{1}{2} dkT[1 - R^2/R_c^2 + \ln(R^2/R_c^2)] \qquad \text{for } R \leqslant R_c. \tag{4}$$

This fact has important consequences when discussing the dynamics of such a constrained idealised polymer chain: the arc length l is not confined to l_{ext} but fluctuates. When averaging l over a time interval which is large compared with the inverse of the fluctuation frequency ν one finds therefore $\langle l \rangle = L/2$. The symmetry of the system is thus restored. The corresponding time averaging or, equivalently, ensemble averaging corresponds to the consideration of the Gibbs entropy where it is summed over all possible configurations with respect to l. The reason why the behaviour discussed in

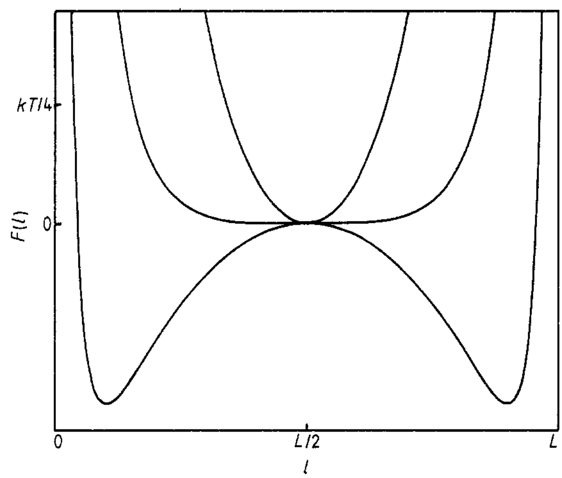

Figure 1. Dependence of the free energy of a random walk system constrained by one slip-link on the arc length that the walk displays between the origin and the slip-link for several values of the real space distance R between the respective points: $R = 1.8R_c$, $R = R_c$, and $R = 0.6R_c$, from top to bottom. (See text for the definition of R_c.)

this letter was not found in previous work on the slip-link and related models [1-5] lies in the fact that those authors were concerned directly with the Gibbs entropy.

For the case $k > 1$ it seems not to be possible to show explicitly in such a simple fashion as above that an instability of the symmetric state (where $l_i = l_0 \equiv L/(k+1)$ holds for all i) occurs. However, in case that $|\boldsymbol{R}_{i+1} - \boldsymbol{R}_i| = R$ holds for all i an investigation of the asymptotic behaviour of the respective PDF $P_k(\{\boldsymbol{R}_i\}; \{l_i\})$ implies that an instability must occur. For that purpose consider the ratio ω of the PDF of an asymmetric state where at least two l_i, l_j exist with $l_i \neq l_j$ to the PDF of the symmetric state. One easily obtains

$$\omega = \left(\prod_{i=1}^{k+1} \frac{l_0}{l_i}\right)^{d/2} \exp\left[-\frac{d}{2}\frac{R^2}{Lb}(k+1)\left(-(k+1) + \sum_{i=1}^{k+1} \frac{l_0}{l_i}\right)\right]. \tag{5}$$

This relation follows from (2) when extended to the case when the RW visits k points in between its two endpoints. For $R \to 0$ it is found that $\omega > 1$ for any asymmetric configuration in the sense defined above. On the contrary, for large R ($R \gg 1$) the exponential dominates the behaviour of ω. Since the bracket in the argument of the exponential is positive for all possible configurations of the arc lengths suspended between the set of points $\{\boldsymbol{R}_i\}$, with the exception of the symmetric distribution, one obtains $\omega < 1$ for large R, i.e. the symmetric distribution is the most probable one. Unfortunately it is not known whether or how R_c is affected by the introduction of several fixed points $\boldsymbol{R}_i$.

Next we study the case where $k = 1$ and $r_1 = |\boldsymbol{R}_1 - \boldsymbol{R}_0| \neq |\boldsymbol{R}_2 - \boldsymbol{R}_1| = r_2$. Using a PDF similar to the one given in (2) we obtain numerically [9] that if r_1 differs not too much from r_2 a bifurcation occurs but this time displaying a profile of $F(l)$ which is asymmetric with respect to $L/2$. The analytical derivation of the value $a_c(R, L) = |r_2 - r_1|_c$ up to which a double minimum potential in F exists is made impossible since it is determined by an equation of sixth order.

In the discussion above it was tacitly assumed that for a specific configuration the visit of the points $\boldsymbol{R}_i$ defines uniquely arc lengths l_i. In two and three dimensions this is of course not the case for the set of walks (in their continuous representation) which visit a given point at least twice is not of measure zero. Furthermore, it might be possible that the observed bifurcation is an artefact which might be due to the use of the Gaussian PDF in (2) because the finite extensibility of a RW with fixed arc length is not respected. This is the reason why a Monte Carlo simulation has been carried out for a RW on $\mathbb{Z}^2$ with fixed endpoints and $k = 1$ intermediate point with distance R from the endpoints through which the chain must pass. As usual, dynamics were introduced to allow for a diffusion through phase space [10]. Again a bifurcation of the type mentioned is observed.

A further point of interest is the question of whether a bifurcation still occurs for chains that do not pass through points but through areas whose centres are fixed at the points $\boldsymbol{R}_i$. This problem cannot be dealt with by use of the method proposed so far due to the self-similar structure of the continuous chain [11]. Note that if one allows for transversal fluctuations of the chain in the areas (or hoops) mentioned above and through which the chain should not pass more than once, one is faced with the problem that—irrespective of how small the area is chosen—when integrating $P_k(\{\boldsymbol{R}_i\}; \{l_i)\}$ over this area configurations are always included where back-tracking of the chain through the hoop is found. Such a repeated threading through a hoop is not consistent with the present formulation of the slip-link model. In order to obtain some insight into this problem a Monte Carlo simulation was done. I choose for the simulation the freely jointed chain [12] being constrained by a hoop with radius αb ($\alpha > 0$) located at $\boldsymbol{R}_1$. Dynamics are introduced in the usual way [13]. The slip-link condition is enforced by the constraint that the part of the chain which passes through the slip-link cannot cross the boundary defining the hoop. Furthermore no segment of the chain except the one threading through the hoop is allowed to cross the area defined by the hoop. Preliminary results (with $N = 17$ and $\alpha = 1$) show that this system exhibits qualitatively the same bifurcational behaviour as the systems with vanishing slip-link diameter discussed above. We conclude that the bifurcation in the constrained RW system is not an artefact which might be due to the vanishing areas of the slip-links as imposed, e.g., in (1) by the delta functions.

Finally, I would like to propose that the constrained RW presented with its bifurcational behaviour might be another interesting example of a simple system exhibiting a bifurcation. Such systems are of some pedagogical value in the field of synergetics [14, 15].

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