I. INTRODUCTION

Creating emergent structures through intelligent engineering of physical interactions between macromolecules is a versatile method to self-assemble or self-organize structures with a target morphology. A particular macromolecular morphology of great interest across disciplines is the helix, as it is a recurring motif across chemistry, biology \cite{1,2} and physics \cite{3,4}. Forging helical structures at the nm to 10μm length scales remain challenging, though helical springs are ubiquitous in NEMS/MEMS devices \cite{5,6} and helical micro-swimmers \cite{7,8} are used for micro-rheology. These helices are produced primarily by various “bottom up approaches” such as vapour deposition which is dependent on the detailed chemistry of the constituent atoms or alternatively using helical templates \cite{9,10} or helices emerge due to suitable confinement effects \cite{11,12}. It would be of interest to devise alternate strategies to obtain spontaneously formed helical architectures at nm–μm length scales using physical forces by approaches which remain independent of chemical details of the monomer constituent.

Here we show emergent helical structures in a (unconfined) bead spring polymeric chain using generic interactions. Our computer simulations unexpectedly show that helical structures can be obtained by inducing instabilities with either Coulomb interactions or other long ranged power law repulsive interactions between monomers starting out from a straight semi-flexible polymeric chain. We discuss two different scenarios where we obtain helical order without the use of torsion inducing potentials or hydrogen-bond mimicking potentials acting between monomers. Thermal fluctuations play a crucial and critical role in the formation of helical structures. In addition, we induce time dependent potentials where the charge of polymer varies with time (say as pH changes with time). As a consequence, helices are formed periodically in phase with the driving, and at intermediate times the semi-flexible chain straightens up.

We use the bead spring model of a polymer for our simulations. The model polymer could be a real polymer, or it can be string of colloids stitched together to form a semi-flexible polymeric chain \cite{23,24}. Thereby, the monomer size and the number of beads (N) in the chain determine the length scale of helices formed. The unit of length in our study is a, where a is the equilibrium length of the harmonic-spring with energy \( U_H = \kappa (r-a)^2 \) between adjacent monomers; r is the distance between monomers with \( \kappa = 20 \times k_B T / (a)^2 \) for Case A with repulsive Coulomb interactions \( U_c = \epsilon_c \times (a/r) \) between the monomers with \( \epsilon_c = 87.2 k_B T \). Case B corresponds to \( \kappa = 10 \times k_B T / (a)^2 \) with the additional interaction between the monomers of the form \( U_d = \epsilon_d \times (a/r)^3 \) with \( \epsilon_d = 107.70 k_B T \) with cutoff at \( r_c = 4.0a \). Diameter of each monomer is \( \sigma = 0.727 a \), and excluded volume (EV) of monomers are modeled by the WCA (Weeks-Chandler-Anderson) potential.

The polymeric chain is semi-flexible; the corresponding bending energy \( U_b = \epsilon_b \cos(\theta) \), where \( \theta \) is the angle between vectors \((-r_i, r_{i+1})\). \( r_i \) is the vector joining monomer i - 1 and its neighbouring monomer i along contour. The thermal energy \( k_B T = 1 \) sets the energy unit. We performed overdamped Brownian dynamics simulations where the friction constant sets the time unit. We observe the polymer dynamics by always starting out from the same straight unstable initial condition (unless specified otherwise): a linear polymer chain of 49 monomers is placed along the y axis with adjacent monomers at a distance of a from each other. The fluctuation dissipation theorem determines the random force on each particle. For studies with cases (A) and (B), we choose \( \epsilon_b = 10 k_B T \) (corresponding to persistence length \( \ell_p = 11a \)) and \( 80 k_B T \), respectively. We use box-size \( \gg 50a \) such that periodic boundary conditions are irrelevant. Hence we do not use Ewald technique to calculate Coulomb interactions as self interactions with periodic images of the monomers are irrelevant.

As the polymer starts out from initial configuration (refer Fig 1b), the thermal and repulsive forces from \( U_d \) (or \( U_c \)) make the linear structure unstable and it forms a kinked structure (Fig 1b). Then the helical conformation emerges at a time \( t \sim \tau \) as seen in Fig 1a before it dissipates away at times \( t >> \tau \) (Fig 1b). The unit time of the problem chosen as \( \tau = (\zeta a^2 / k_B T) \), the time taken for a isolated monomer particle to diffuse a distance of a. Random fluctuations due to \( k_B T \) play a crucial rule in de-
along stretches out but never forms helices as all the forces are using 49 monomers at time \( t = 3.3 \times 10^{-3} \tau \). (c) Snapshot of the subsequent helix formed using 49 monomers at time \( t = \tau \) and (d) unwinding of the helix formed by 49 monomers at time \( t = 5\tau \). The corresponding snapshots with potential \( U_d \) are in the supplementary.

Development of the helical order though \( \epsilon_c, \epsilon_d \) and \( \kappa, \epsilon_b \) are all \( \gg k_B T \). A straight polymer configuration at \( T = 0 \) stretches out but never forms helices as all the forces are along \( y \) axis. Movies S1, S2 helps visualize the instability for Case-A \& case-B, respectively, and movie S3 is for Case B with \( k_B T = 0 \) (refer Supplementary).

We quantify the emergence of helicity as a function of time by calculating and plotting two quantities in Fig 2, the global order parameter \( H4 \) and the local order parameter \( H2 \) where,

\[
H4 = \frac{1}{N-2} \left( \sum_{i=2}^{i=N-1} \mathbf{u}_i \right)^2; H2 = \frac{1}{N-3} \left( \sum_{i=2}^{i=N-2} \mathbf{u}_i \cdot \mathbf{u}_{i+1} \right)
\]

(1)

where \( \mathbf{u}_i \) is the unit vector of \( \mathbf{U}_i = \mathbf{r}_i \times \mathbf{r}_{i+1} \). A perfect helix in the continuum picture with infinitesimal vectors \( \mathbf{r}_i, \mathbf{r}_{i+1} \) vectors will have vectors \( \mathbf{u}_i \) pointing along the helix axis and hence will have a high value of \( H4 \). However, if one obtains a helical structure where half of the chain is right handed, and the rest of it is left-handed, \( H4 \) will be zero. Hence, we need the other parameter \( H2 \) to identify local helical order and one needs to obtain finite values of both \( H4 \) and \( H2 \) to identify the presence of a helix $^{[2, 27]}$. A simple semi-flexible polymer chain \((U_c = 0 \& U_d = 0)\) shows \( H2, H4 \) values close to 0 as expected for a chain bent due to thermal fluctuations. But the polymers with additional interactions \( U_c \) or \( U_d \) lead to the formation of transient helices with finite values of \( H2, H4 \). The time taken for the helix to form is \( \approx 0.5\tau \). We also investigated the emergence of helices for chains of 25 and 100 monomers, respectively (refer supplementary). A chain of 100 monomers has approximately 5 helical segments and thereby has relatively lower values of \( H4 \) since it may have different segments of opposing handedness.

But why are the helices formed by the semi-flexible chains in the presence of spherically symmetric repulsive potentials \( U_c \) or \( U_d \)? What role does temperature play?

After time \( t = 0 \), the thermal kicks shift the position of particles from a straight line initial condition: this is accentuated by the repulsive \( U_c \) (or \( U_d \)) which gets the polymer to additionally stretch out and increase the distances between monomers. This in turn leads to increase of \( U_H \) and \( U_b \) leading to an unstable kinked structure (Fig 1b). Thereafter, the repulsive interaction further forces the \( i \) th monomer to move out of the plane formed by monomer-triplets of \( i, i+1, i+2 \) to reduce repulsive energy \( U_b \) (or \( U_d \)) at the cost of increasing \( U_H \) and \( U_b \), which gives rise to a net torsion. In turn, the \( i' = i + 1 \)-th monomer repels and pushes the \( i' + 3 \) monomer out of the plane of \( i', i' + 1, i' + 2 \) monomers and the instability propagates along the chain and leads to a maximum in \( U_b \).
and $U_H$ at $\approx 0.1\tau$. Subsequently, this structure evolves to form helical structures at time $\tau$ to lower both $U_c$ and $U_b$ such that the bending is gradual over the length of the polymer. However, even gentle, uniform bends are penalized by $U_b$ and hence at times $t > 2\tau$ the uniform helical structures start to gradually locally unwind. This can be understood by looking at the energies $U_c, U_b$ and $U_h$ per particles versus time in Fig. 3.

Thermal fluctuations play a crucial role in development of the helical order. At $T = 0$, starting from a straight polymer initial configuration along $\hat{y}$, the polymer stretches out but never forms helices as forces arising from $U_c$ (or $U_d$) and $U_H$ act along the line joining the centres of the monomers. At $T > 0$, thermal fluctuations introduce deviations in positions away from the straight line, which leads to forces along the $\hat{x}$ and the $\hat{z}$ directions, which in turn lead to the emergence of helical conformations when $U_c \neq 0$ (or $U_d \neq 0$). To test this, we ran a simulation at temperature $T = 0$ starting from a uniformly curved initial condition such that the chain forms an arc in $x-y-z$ plane (details in supplementary).

Such an initial conformation again leads to helical instabilities due to forces along the $x$ axis and the $z$ axes. This is substantiated by data in Fig. 3, for $U_c$ and $U_d$. Alternatively, starting from an initial conformation with small random displacements along $x$ and $z$ coordinates of the particles we still obtain a helical conformation at temperature $T = 0$ as seen in Fig. 3. Since the helical instabilities are triggered by random fluctuations due to thermal noise at finite $k_B T$, we do not have any control on the handedness of the chain.

We emphasize that the balance of all the three interactions play a critical role in the formation of the helices. If the soft spring ($\kappa = 20 k_B T / \langle a \rangle^2$ or $\kappa = 10 k_B T / \langle a \rangle^2$) joining monomers becomes too stiff then the position of monomers do not time-evolve to form a helix in response to forces arising from $U_c$ and $U_d$. For high values of $\kappa$, stiff springs do not permit the $i + 3$-th monomer to move away from the plane formed by the positions of $i, i + 1, i + 2$ monomers, thus preventing helix formation, refer Figs. 4.a,d for corresponding data. Increase in the value of $\epsilon_c$ in $U_c$ (or $\epsilon_d$ in $U_d$) increases propensity of helix formation as observed in the increase in the value of $< H_2 >$ with $\epsilon_c$ in Figs. 4.b,e. At higher values of $\epsilon_c, \epsilon_d, < H_2 >$ saturates. A higher value of $\epsilon_b$ in $U_b$ hinders the formation of kinks that subsequently give rise to the helical structures, thereby, suppressing the instability: refer Figs. 4.c,f. Thus only in a certain range of these interactions of $U_c$ (or $U_d$) and $U_b$ do we obtain helices as shown in the state diagrams Figs. 4.g,h for the two cases. To obtain Figs. 4.g,h, we systematically varied the strength of the interactions by varying $\epsilon_c$ ($\epsilon_d$) and $\epsilon_b$ and identify the structure as a helix only if the value of $< H_2 >$ is greater than 0.2.

What determines the pitch of the helix and how can we control it? The procedure for calculating the pitch (in units of monomers) is detailed in the supplementary section. Once formed, the pitch of the helix increases with time as the helical structure formed gradually unwinds.
over time to decrease bending energy costs. To that end, we show the variation of pitch versus time in Fig.5a for a chain length of $N = 100$ monomers for semiflexible polymer with $U_c$ acting between the monomers. A polymer with large $N$ is chosen so that the pitch can be better calculated. The pitch increases with increasing $\epsilon_c$ (refer Fig.5b) as a higher value of $\epsilon_c$ results in a higher energy cost associated with the local bends along the polymer chain. Thus a higher value of $\epsilon_c$ gives rise to fewer loops along the chain, or a higher value of pitch. We did not observe any significant dependence of the pitch on $\kappa$ and $\epsilon_c$ (or $\epsilon_d$). The corresponding data for the helix pitch versus $\epsilon_c$ is given in the supplementary.

As we saw earlier, that the formation of the helix depends on the strength of the Coulomb interaction $\epsilon_c$, or on the value of $\epsilon_d$. If the distance between monomers is $a = 10 nm$, then at $T = 300K \epsilon_c = 727 k_B T$ corresponds to a charge of $\approx -1e$ at physiological pH. The question is if the value of $\epsilon_c$ in the model polymer chain increases with time, i.e. a neutral semi-flexible chain becomes charged (e.g. due to change in pH), does the polymer form a helix starting out from a relatively straight initial configuration?

To that end, we use a time dependent potential of the form $U_c(t) = \epsilon_c(t) (a/r)$ where $\epsilon_c(t) = \epsilon_0^c (cos(2\pi t/T_0))^2$ where $T_0 = 0.13\tau$, $\epsilon_0^c = 727.3 k_B T$ and $t$ denotes the simulation time. The values of $\epsilon_0$ and $\kappa$ was changed to $700 k_B T$ & $1500 k_B T/(a/r)^2$, respectively, to have a stiffer chain. We observe that we obtain helices, recurringly. The helices form, then dissolve away such that the polymer becomes straight as $\epsilon_c(t)$ becomes zero, and then form again. To substantiate that we show $H2$ for a chain of 49 monomers under the influence of $U_c(t)$ and also for a chain of 49 monomers such that $U_c = 0$ in Fig.5b. We also show data for the same values of $\kappa$ and $\epsilon_b$ but $U_d(t) = (769.34 (a/r)^3) (cos(2\pi t/T_0))^2$ in Fig.5b, where again we obtain helices recursively. The helices formed for these high values of $\kappa$ and $\epsilon_b$ dissolve away very quickly hence, we choose relatively low values of $\kappa$ and $\epsilon_b$ for comparison of response.

In conclusion, we demonstrate that spherically symmetric long ranged repulsion can give rise to helices in a semiflexible polymer, which we find to be completely non-intuitive apriori. There have been previous reports of extremely short lived helix formation in polymers in bad solvents undergoing collapse due to hydrophobic forces which act at nm length scales. Others have observed helices on optimally packing tubular filaments at a particular ratios of pitch and radius. But the authors comment that compaction of a chain of spheres gives very different results from compaction of a tube. We believe our study is the first report of the self-emergence of free standing helical structures using the most generic of potentials which could have profound influence in understanding emergence of such structures at nm-$\mu$ length scales, in a variety of situations within the living cell or outside. This is a consequence of the long range of the interactions used which makes the $i + 3$-th monomer move out of plane to increase the distance between them. Importantly, we have considered the charges on the polymer chains to be unscreened by counterions. Our proposed mechanism can be used to design helical springs for NEMs/MEMs devices at length scales and using material of choice by arresting the relaxation process at a suitable time.

We thank K Guruswamy and Bipul Biswas for useful discussions. We used of computer cluster obtained using DBT Grant BT/PR16542/BID/7/654/2016 to AC. AC acknowledges funding by DST Nanomission, India, the Thematic Unit Program (Grant No. SR/NM/TP-13/2016) and discussions in Stat-physics meetings in ICTS, Bangalore, India.
[1] Jayanth R. Banavar, Trinh X. Hoang, Amos Maritan, Flavio Seno, and Antonio Trovato. Unified perspective on proteins: A physics approach. *Physical Review E*, 70(4), October 2004.

[2] S. J. Gerbode, J. R. Puzezy, A. G. McCormick, and L. Mahadevan. How the cucumber tendril coils and overwinds. *Science*, 337(6098):1087–1091, August 2012.

[3] Y. Forterre and J. Dumais. Generating helices in nature. *Science*, 333(6050):1715–1716, September 2011.

[4] Amos Maritan, Cristian Micheletti, Antonio Trovato, and Jayanth R. Banavar. Optimal shapes of compact strings. *Nature*, 406(6793):287–290, July 2000.

[5] B. Pokroy, S. H. Kang, L. Mahadevan, and J. Aizenberg. Self-organization of a mesoscale bristle into ordered, hierarchical helical assemblies. *Science*, 332(5911):237–240, January 2009.

[6] Sid Ahmed Sabeur, Fatima Hamdache, and Friederike Schmid. Kinetically driven helix formation during the homopolymer collapse process. *Physical Review E*, 77(2), February 2008.

[7] Huaping Li and Alkan Kabakcioglu. Role of helicity in DNA hairpin folding dynamics. *Physical Review Letters*, 121(13), December 2018.

[8] Daniel A. Vega, Andrei Milchev, Friederike Schmid, and Mariano Febbo. Anomalous slowdown of polymer detachment dynamics on carbon nanotubes. *Physical Review Letters*, 122(21), May 2019.

[9] Gaoshan Huang and Yongfeng Mei. Helices in micro-world: Materials, properties, and applications. *Journal of Materionics*, 1(4):296–306, December 2015.

[10] Pu Xian Gao, Wenjie Mai, and Zhong Lin Wang. Superaelasticity and nanostructure mechanics of ZnO nanohelices. *Nano Letters*, 6(11):2536–2543, November 2006.

[11] Soichiro Tottori, Li Zhang, Famin Qiu, Krzysztof K. Krawczyk, Alfredo Franco-Obregon, and Bradley J. Nelson. Magnetic helical micromachines: Fabrication, controlled swimming, and cargo transport. *Advanced Materials*, 24(6):811–816, January 2012.

[12] Ambarish Ghosh and Peer Fischer. Controlled propulsion of artificial magnetic nanostructured propellers. *Nano Letters*, 9(6):2243–2245, June 2009.

[13] Li Zhang, Jake J. Abbott, Lixin Dong, Kathrin E. Peyer, Bradley E. Kratovich, Haixin Zhang, Christos Bergeles, and Bradley J. Nelson. Characterizing the swimming properties of artificial bacterial flagella. *Nano Letters*, 9(10):3663–3667, October 2009.

[14] Li Zhang, Kathrin E. Peyer, and Bradley J. Nelson. Artificial bacterial flagella for micromanipulation. *Lab on a Chip*, 10(17):2203, 2010.

[15] Yong Wang, Jun Xu, Yawen Wang, and Hongyu Chen. Emerging chirality in nanoscience. *Chem. Soc. Rev.*, 42(7):2930–2962, 2013.

[16] W. Wang, K. Yang, J. Gaillard, P. R. Bandaru, and A. M. Rao. Rational synthesis of helically coiled carbon nanowires and nanotubes through the use of tin and indium catalysts. *Advanced Materials*, 20(1):179–182, January 2008.

[17] Hai-Feng Zhang, Chong-Min Wang, and Lai-Sheng Wang. Helical crystalline SiC/SiO2core-shell nanowires. *Nano Letters*, 2(9):941–944, September 2002.

[18] Hai-Feng Zhang, Chong-Ming Wang, Edgar C. Buck, and Lai-Sheng Wang. Synthesis, characterization, and manipulation of helical SiO2nanosprings. *Nano Letters*, 3(5):577–580, May 2003.

[19] Lichun Liu, Sang-Hoon Yoo, Sang A. Lee, and Sungho Park. Wet-chemical synthesis of palladium nanosprings. *Nano Letters*, 11(9):3897–3982, September 2011.

[20] K. Robbie, D. J. Broer, and M. J. Brett. Chiral nematic order in liquid crystals imposed by an engineered inorganic nanostructure. *Nature*, 399(6738):764–766, June 1990.

[21] K. Robbie, M. J. Brett, and A. Lakhtakia. Chiral sculptured thin films. *Nature*, 384(6610):616–616, December 1996.

[22] D. C. Rapaport. Molecular dynamics simulation of polymer helix formation using rigid-link methods. *Physical Review E*, 66(1), July 2002.

[23] Debasish Chaudhuri and Bela M. Mulder. Spontaneous helicity of a polymer with side loops confined to a cylinder. *Physical Review Letters*, 108(26), June 2012.

[24] Sunita Sanwaria, Sajan Singh, Andriy Horechyy, Petr Formanek, Manfred Stamm, Rajiv Srivastava, and Bhanu Nandan. Multifunctional core–shell polymer–inorganic hybrid nanofibers prepared via block copolymer self-assembly. *RSC Advances*, 5(109):89861–89868, 2015.

[25] Bipul Biswas, Raj Kumar Manna, Abhrarajit Laskar, P. B. Sunil Kumar, Roncojoy Adhikari, and Guruswamy Kumaraswamy. Linking catalyst-coated isotropic colloids into “active” flexible chains enhances their diffusivity. *ACS Nano*, 11(10):10025–10031, September 2017.

[26] Guruswamy Kumaraswamy, Bipul Biswas, and Chandan Kumar Choudhury. Colloidal assembly by ice templating. *Faraday Discussions*, 186:61–76, 2016.

[27] J. P Kemp and J. Z. Y Chen. Folding dynamics of the helical structure observed in a minimal model. *Europhysics Letters (EPL)*, 59(5):721–727, September 2002.