Entropy-driven orientational hopping in a magnetically confined colloidal rod

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We report the novel orientational hopping behaviour of a passive colloidal ferromagnetic rod under the influence of a static external magnetic field. In the zero-field limit, the rod tends to lie horizontally in the plane and undergoes azimuthal thermal reorientation, while gravity exponentially suppresses large thermal deviations in inclination. A horizontal magnetic field acts to trap the rod, confining its azimuthal angle to maximise alignment of the magnetic moment with the field. However, we observe a significant emergence of a tendency for the rod to reorient vertically despite a corresponding increase in total potential energy of ~ 3 k$_BT$. We provide a thorough statistical mechanical analysis of the system by deriving the Boltzmann distribution across rod orientations which shows the emergence of the metastable vertical state; the histogram of angle data is in good qualitative agreement with the analytic probability distribution —both show a probability-minimum at an intermediate angle somewhere between the vertical and horizontal states. We show that this is in fact an entirely entropic process and discuss the generic physics involved in the stabilisation of a state whose potential energy is intuitively a maximum.

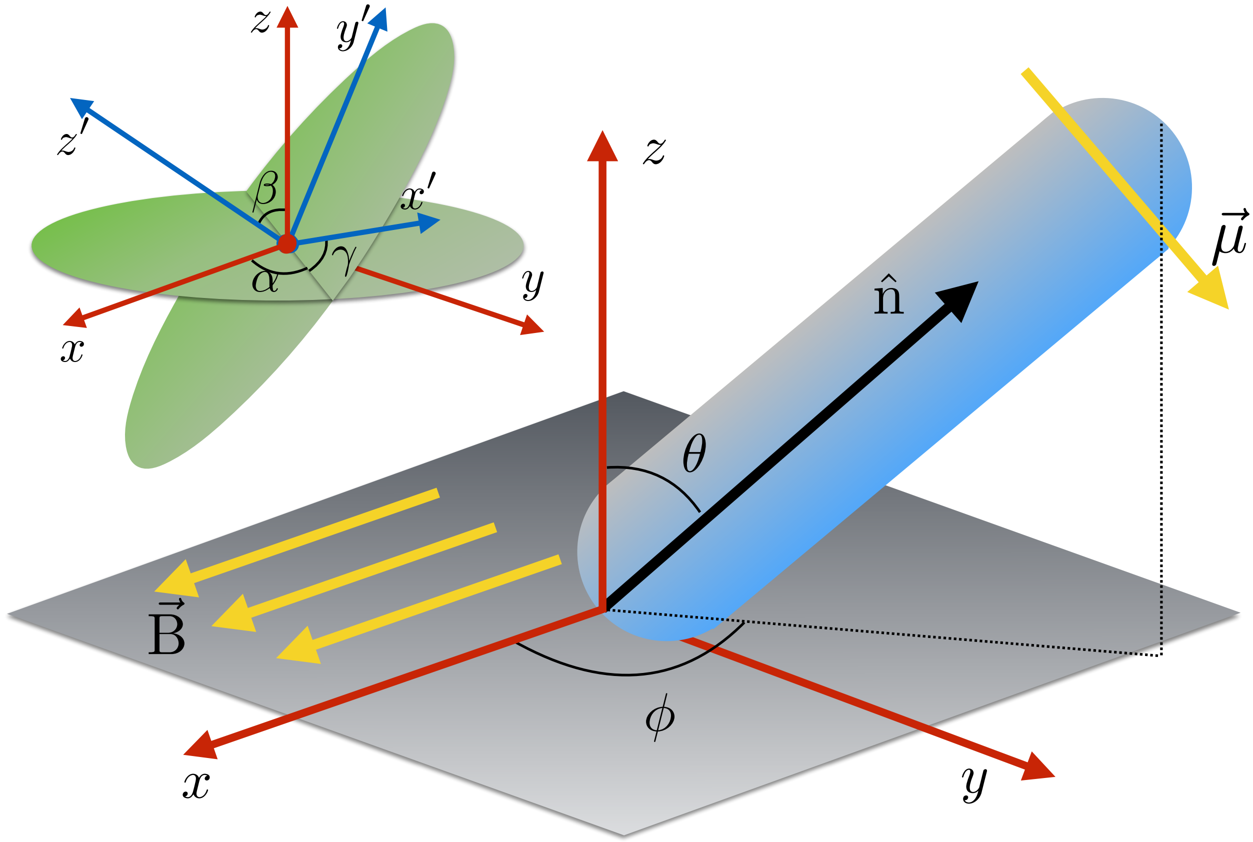
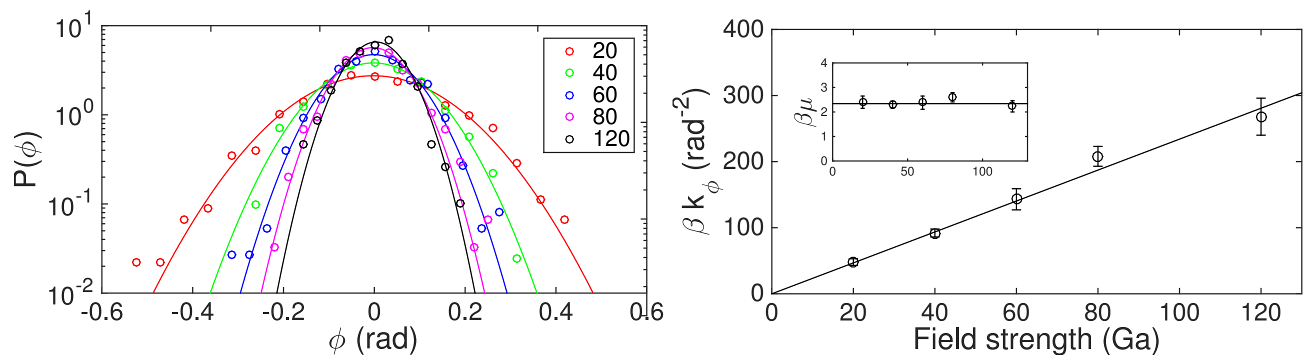


FIG. 1: *Main:* Geometry and notation used throughout. The orientation of the rod, $\hat{\mathbf{n}}$ is defined as the unit vector pointing along the long axis of the rod in the +ve z-direction. This makes an angle θ with the z-axis and its projection in the xy-plane subtends an angle ϕ with the x-axis. A perpendicular permanent magnetic moment $\boldsymbol{\mu}$ is embedded in one of the caps and rotates rigidly with the rod. An external magnetic field $\mathbf{B}$ is applied in the x-direction while the gravitational field acts in the $-$ve z-direction. *Inset:* Euler angles are useful for describing the fixed-body rotation of the rod, where $\hat{\mathbf{n}} = \hat{\mathbf{z}}'$, $\boldsymbol{\mu} = \mu\hat{\mathbf{x}}'$, $\beta = \theta$, and $\alpha = \phi + \frac{\pi}{2}$.



(a)

(b)

FIG. 2: (a) Probability distribution of the azimuthal angle of deviation $\phi - \phi_0$ of the rod from alignment with a static magnetic field. The data appear to be distributed normally with a spread $\langle\phi^2\rangle$ obtained by applying a Gaussian fit. (b) The equipartition theorem states $\frac{1}{2}k_\phi\langle\phi^2\rangle = \frac{1}{2}\mathrm{k}_B T$ where $k_\phi = \mu B$ is the stiffness of the torsional trap. We make use of this to show that $\mathrm{k}_B T/\langle\phi^2\rangle$ increases linearly with B, in other words, μ remains constant (see inset) across the range of field strengths used.

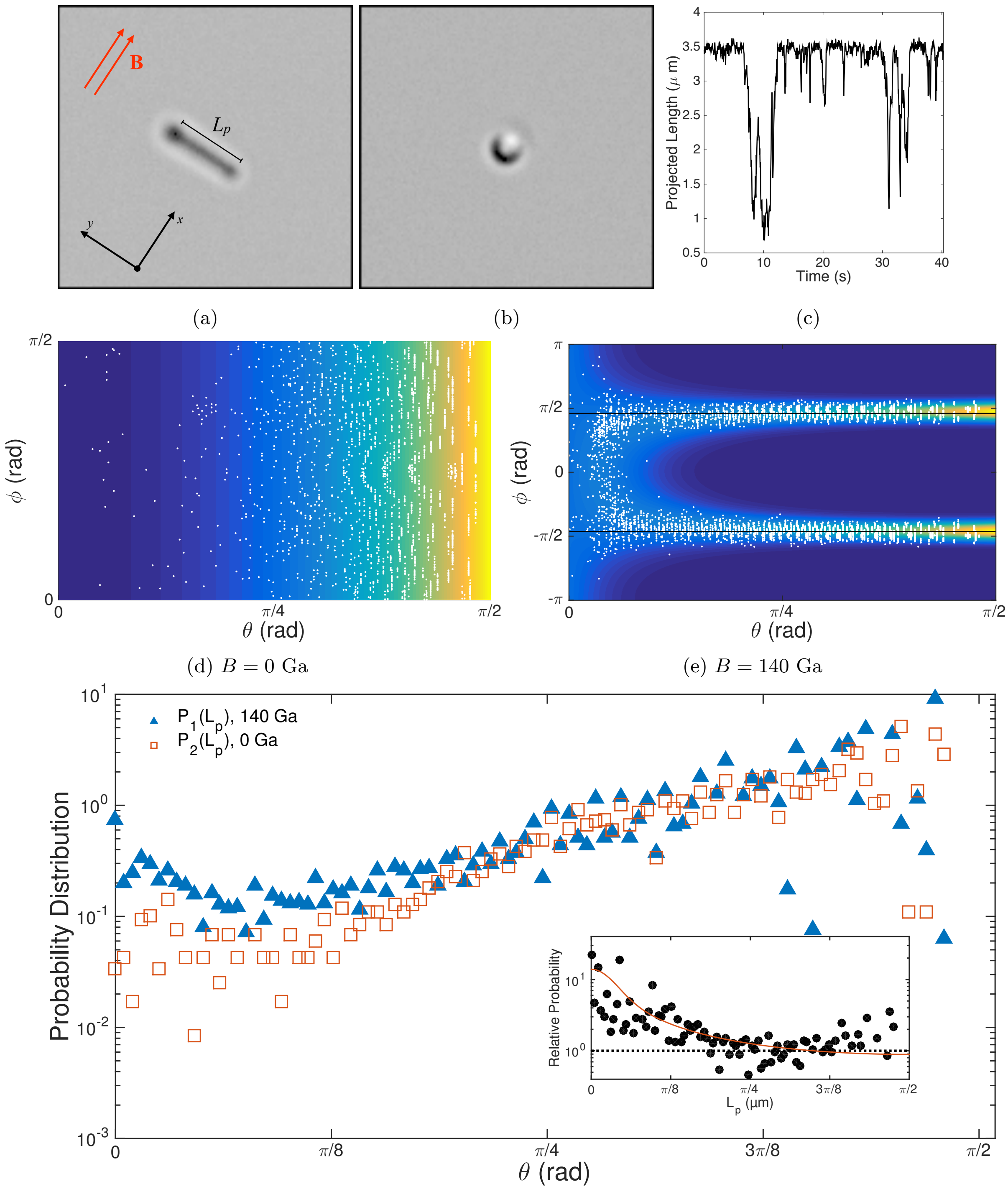


FIG. 3: (a-b) A magnetic field in the x-direction is responsible for the trapping of the rod in the yz-plane; we observe the rod to hop between two states: (a) horizontally along $\pm x$ with $\theta = \pi/2$, and (b) vertically along z, where $\theta = 0$. (c) A short segment of projected length $L_p(t)$ demonstrates the 'hopping' nature of this behaviour. (d-e) The distributions of $\theta(t)$-$\phi(t)$ data falls on top of the theoretically predicted distributions $P(\phi, \theta)|_{B=0,140\ \mathrm{Ga}}$. The trapping angle of the rod $|\phi_0| = (82.8 \pm 0.2)^{\circ} < \pi/2$ suggests that the magnetic moment is not quite perpendicular to the rod, making an angle $\epsilon = (7.2 \pm 0.2)^{\circ}$ with cross-sectional plane. The radial pattern in the data is an artefact of propagating the measured projected length, L_p, through an inverse sine function in the calculation of θ (f) Histogram of $L_p(t)$ over 60 minutes shows a markedly increased tendency for vertical states ($L_p \approx 1\mu$m) to be realised when a magnetic field is present (blue) with respect to a free rod, under no magnetic field (red).

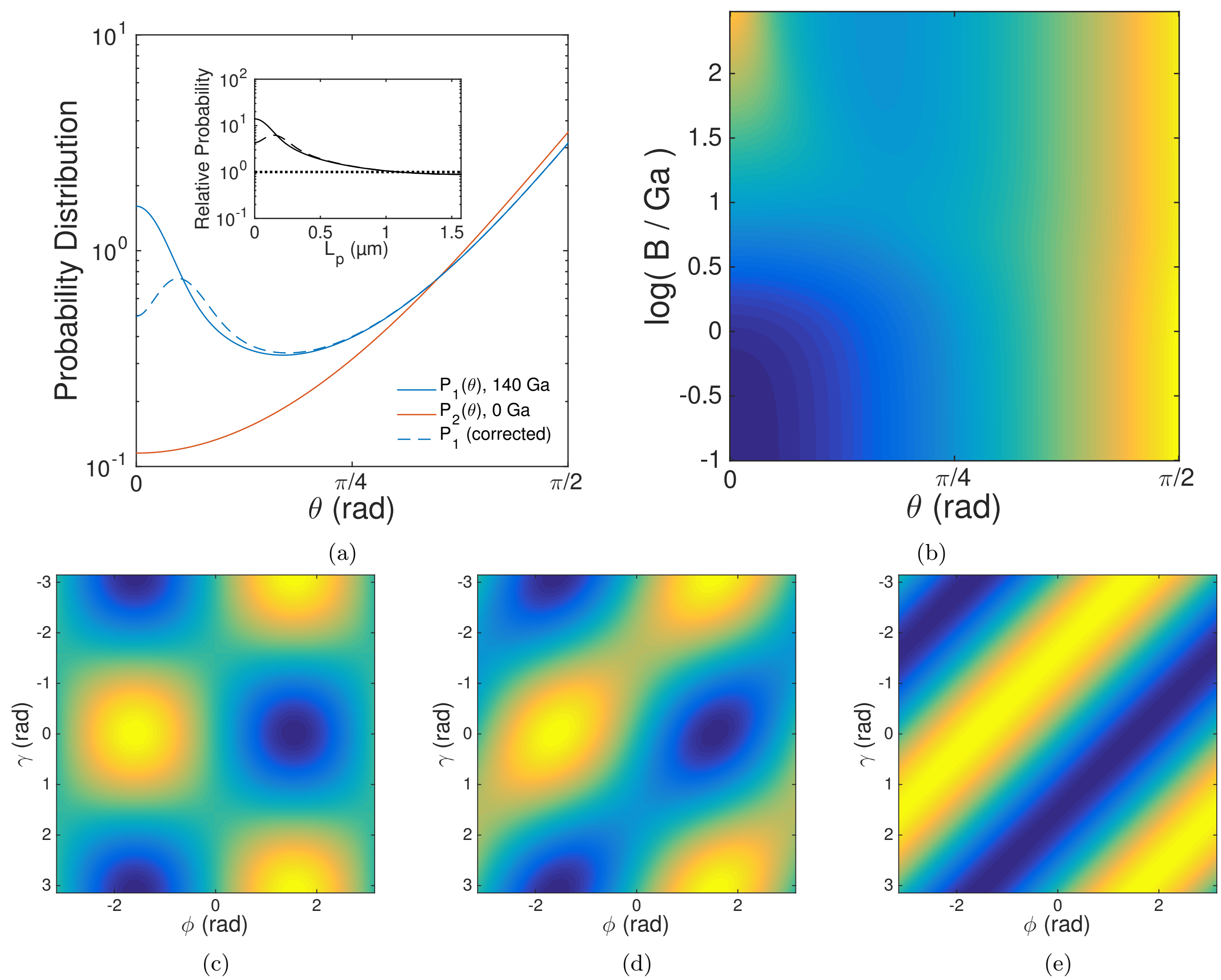


FIG. 4: (a) Probability distribution for a rod with $\mu = 1.2\mathrm{k}_B T/Ga$ in 140 Ga (blue) and 0 Ga (red) fields shows an emergent bistability between vertical and horizontal states brought on by the external field for an ideal rod (—) and one where $\boldsymbol{\mu}$ is offset from the cross-sectional plane by $\epsilon = 7°$ (- -). Inset: Relative likelihood ratio between both probability distributions. (b) Same as (a) but for varying magnetic fields. (c-e) The energy $U(\phi, \theta, \gamma)$ for three polar angles $\theta = \frac{\pi}{2}, \frac{3\pi}{8}, \frac{\pi}{20}$ shows the loss of a degree of freedom. When the rod is lying flat, ϕ and γ are independently constrained, but when vertical only the sum $\phi + \gamma$ is constrained. This results in the entropic favouring of vertical states compared to intermediate states despite the gravitational cost of standing up.