

Spiral trajectories of asymmetric molecules

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SPECIAL TOPIC — A celebration of the 90th Anniversary of the Birth of Bolin Hao

Spiral trajectories of asymmetric molecules

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Spiral patterns widely exist in both macroscopic and microscopic systems such as hearts, bacteria, and active matters but have never been reported at molecular length scale. The emergence of spiral patterns has considerable impacts on the trajectories of the objects and thus usually relates to various physical, chemical, biological and physiological processes. In this paper, we show that, down to the length scale of only several Angstroms, asymmetric molecules exhibit spiral patterns in their trajectories within finite time based on the under-damped Langevin equation and demonstrated by molecular dynamics simulation. The key to this observation lies in the asymmetric molecular architecture that leads to a translation–rotation coupling. This finding enriches the knowledge of spiral patterns to the molecular length scale, provides a new insight into the understanding of various processes at the molecular level, and may evoke new ideas on the understanding of the vortices in turbulence.

Keywords: spiral pattern, asymmetric molecule, under-damped Langevin equation, translation–rotation coupling

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1. Introduction

Spiral patterns widely exist in macroscopic systems, such as the spiral waves in heart ventricular fibrillation,[1,2] spiral collective movement of fish shoals,[3] spiral eddies in turbulence,[4,5] and even spiral galaxies.[6] The spiral is characterized by a bending direction that generally originates from symmetry breaking. The emergence of spiral patterns has considerable impacts on the trajectories of the objects and thus usually relates to various physical,[7,8] chemical,[9,10] biological[11–15] and even physiological processes.[16,17] For example, the spiral pattern in the electrical conduction system of the heart causes cardiac arrhythmia and may result in cardiac arrest.[17,18] Spiral patterns have also been observed in microscopic systems including microtubules[11,12] and bacterial suspension.[13–15] Recently, understanding and designing microscale active matters have attracted continuously increasing attention with the development of nanoscience and nanotechnology.[19–27] One of the most typical features of active matters is the spiral patterns in their trajectories.[27,28] However, to the best of our knowledge, in the systems at molecular length scale, there has been no report on the spiral pattern.

In this paper, we show that, down to the length scale of only several Angstroms, asymmetric molecules exhibit spiral pattern in their trajectories based on under-damped Langevin equation. The key to this observation lies in the asymmetric architecture of the molecules that leads to a coupling between their translational and rotational motions. For an asymmetric molecule, the collision forces acted by surrounding molecules have moment arms of different lengths to its center of mass (CoM) and the imbalanced torques give rise to the spiral trajectories. We also carry out molecular dynamics simulation of a model asymmetric molecule to demonstrate such spiral trajectories. It should be noted that the spiral patterns in the trajectories only occur within finite time interval before the onset of random diffusive regime since it solely results from thermal fluctuations without any input of external energy. Our finding enriches the knowledge of spiral patterns to the molecular length scale, provides a new insight for the understanding of various fast physical, chemical, biological and physiological processes and may evoke new ideas on the understanding of the vortices in turbulence.

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2. Theoretical derivation

We employ the under-damped Langevin equation

$$m_i\dot{\boldsymbol{v}}_i = -\lambda_i \boldsymbol{v}_i + \boldsymbol{\zeta}_i + \boldsymbol{f}_i \tag{1}$$

to describe the motion of atom i in a target molecule with any shape under thermal fluctuations, where $\boldsymbol{v}_i$ and m_i are the velocity and mass of the atom, respectively. The first term on the right-hand side of Eq. (1) is the resistive force based on Stokes' law with the resistance coefficient λ_i. The second term $\boldsymbol{\zeta}_i$ is a white noise representing the effect of the collisions with surrounding molecules, and the last term $\boldsymbol{f}_i$ is the internal force acting on atom i by other atoms in the same molecule via covalent bonding. We consider the molecule as a rigid object. It follows

$$\boldsymbol{v}_i = \boldsymbol{v} + \boldsymbol{\omega} \times \boldsymbol{r}_i, \tag{2}$$

where $\boldsymbol{v}$ is the translational velocity and $\boldsymbol{\omega}$ is the angular velocity of the CoM of the molecule. $\boldsymbol{r}_i$ is the relative position vector from the CoM to atom i. Summing up the Langevin equations, Eq. (1), of all atoms in the molecule renders

$$m\dot{\boldsymbol{v}} = -\lambda \boldsymbol{v} + \boldsymbol{\zeta} - \lambda \boldsymbol{\omega} \times \boldsymbol{R} \text{ with } \boldsymbol{R} = \frac{\sum_i \lambda_i \boldsymbol{r}_i}{\sum_i \lambda_i}, \tag{3}$$

where $m = \sum_i m_i$, $\lambda = \sum_i \lambda_i$, $\boldsymbol{\zeta} = \sum_i \boldsymbol{\zeta}_i$, and $\sum_i \boldsymbol{f}_i = 0$ because the sum of all internal forces in the molecule is zero. The rotational Langevin equation is written as

$$\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{I}\cdot\boldsymbol{\omega}) = -\boldsymbol{J}\cdot\boldsymbol{\omega} + \boldsymbol{\zeta}_r - \lambda \boldsymbol{R} \times \boldsymbol{v}, \tag{4}$$

where the inertia tensor of the rigid object $\boldsymbol{I} = \sum_i m_i(r_i^2\boldsymbol{E} - \boldsymbol{r}_i\boldsymbol{r}_i)$, the rotational damping tensor $\boldsymbol{J} = \sum_i \lambda_i(r_i^2\boldsymbol{E} - \boldsymbol{r}_i\boldsymbol{r}_i)$, the moment of noise $\boldsymbol{\zeta}_r = \sum_i(\boldsymbol{r}_i \times \boldsymbol{\zeta}_i)$ and $\sum_i(\boldsymbol{r}_i \times \boldsymbol{f}_i) = 0$ because the sum of the moments of internal forces is also zero. Here $\boldsymbol{E}$ is a unit tensor.

In the case of two-dimensional (2D) motion, Eqs. (3) and (4) can be simplified as

$$m\dot{v}_x = -\lambda v_x + \zeta_x + R\lambda\omega\sin\theta,$$
$$m\dot{v}_y = -\lambda v_y + \zeta_y - R\lambda\omega\cos\theta, \tag{5}$$
$$I_z\dot{\omega} = -J_z\omega + \zeta_z + R\lambda\left(v_x\sin\theta - v_y\cos\theta\right), \tag{6}$$

where $I_z = \sum_i m_i(x^2+y^2)$ and $J_z = \sum_i \lambda_i(x^2+y^2)$. R is the magnitude of the vector $\boldsymbol{R}$ and θ is the angle between $\boldsymbol{R}$ and the x-axis, which denotes the orientation of the molecule.

Define a function

$$T(t) = 1 - \exp\left(-\frac{t}{\tau}\right), \tag{7}$$

and a functional

$$A\{g(s)\} = \frac{R}{\tau}\int_0^t \left[\langle g(s)\rangle_\zeta - \frac{1}{\tau}\int_0^s \langle g(s')\rangle_\zeta \times \exp\left(\frac{s'-s}{\tau}\right)\mathrm{d}s'\right]\mathrm{d}s, \tag{8}$$

with $\tau = m/\lambda$ being the characteristic time for the relaxation of the inertia. The average runs over all samples with different ζ. From Eq. (5), we can obtain the mean trajectory as

$$\langle x(t)\rangle_\zeta = (v_{0x}\tau + R\cos\theta_0)\,T(t) - A\{\cos\theta(s)\},$$
$$\langle y(t)\rangle_\zeta = (v_{0y}\tau + R\sin\theta_0)\,T(t) - A\{\sin\theta(s)\}, \tag{9}$$

where v_{0x}, v_{0y} are the initial velocities and θ_0 is the initial orientation angle of the molecule at time $t = 0$. Equation (6) is difficult to solve directly. Considering that the molecule is not far from a symmetric shape and R is a small parameter, equation (6) becomes a classical rotational Langevin equation plus the "first-order" perturbation correction of R. We can obtain the mean values of sines and cosines from an initial solution of the classical rotational Langevin equation (detailed derivation given in SM[29]):

$$\langle\cos\theta(t)\rangle_\zeta = \cos[\theta_0 + \omega_0\tau_r T(t)]\,W(t),$$
$$\langle\sin\theta(t)\rangle_\zeta = \sin[\theta_0 + \omega_0\tau_r T(t)]\,W(t), \tag{10}$$

with $W(t) = \exp\{D_r t + D_r\tau_r T(t)[2 + T(t)]/2\}$. Here ω_0 is the initial angular velocity at $t = 0$, $\tau_r = I_z/J_z$ is the characteristic time for the relaxation of the rotational inertia and $D_r = k_\mathrm{B}T/J_z$ is the rotational diffusion coefficient.

Considering that $\boldsymbol{v}_0$ has an isotropic distribution, $\langle v_{0x}\rangle = 0$ and $\langle v_{0y}\rangle = 0$. The average of Eq. (9) over all $\boldsymbol{v}_0$ becomes

$$\langle x(t)\rangle_{\zeta,\boldsymbol{v}_0} = R\cos\theta_0 T(t) - A\{\cos\theta(s)\},$$
$$\langle y(t)\rangle_{\zeta,\boldsymbol{v}_0} = R\sin\theta_0 T(t) - A\{\sin\theta(s)\}. \tag{11}$$

In the long-time limit, $T(t)$ approaches unity and $W(t)$ vanishes, giving

$$\langle x(t)\rangle_{\zeta,\boldsymbol{v}_0} = R\cos\theta_0,$$
$$\langle y(t)\rangle_{\zeta,\boldsymbol{v}_0} = R\sin\theta_0, \tag{12}$$

indicating that as $t \to \infty$, the mean trajectory converges to the endpoint of the vector $\boldsymbol{R}$ at $t = 0$. Furthermore, since θ_0 also has an isotropic distribution, the average of Eq. (11) over all θ_0 values becomes zero:

$$\langle x(t)\rangle_{\zeta,\boldsymbol{v}_0,\theta_0} = 0, \quad \langle y(t)\rangle_{\zeta,\boldsymbol{v}_0,\theta_0} = 0. \tag{13}$$

Figures 1(a)–1(d) present the predictions of Eq. (11) on the mean trajectories of an asymmetric molecule without particularly assumed shape. Clearly, the trajectories display spiral patterns which separate from each other, depending on the initial orientation θ_0 of the molecule. The parameters are set to be $R = 0.1$ nm, $\tau = 0.2$ ps, $\tau_r = 0.8$ ps, $D_r = 2.4$ rad^2/ps and $\omega_0 = 2.0$ rad/ps, 0.8 rad/ps, 0.3 rad/ps and 0 rad/ps, respectively. The spirals have a right-hand chirality for positive ω_0 and left-hand chirality for negative ω_0 (shown in SM[29]).

For $\omega_0 = 0$, as presented in Fig. 1(d), we can see an aster pattern without chirality. Moreover, a larger ω_0 corresponds to a larger curvature of the spiral trajectory.

The spiral patterns of the trajectories show a centrosymmetric geometry. Physically, θ_0 has an isotropic distribution. If we run an ensemble average over all possible θ_0 values, Eq. (11) predicts that there is no net mean displacement of the molecule CoM, which is consistent with the conventional diffusion theory. We also would emphasize that the key to the spiral trajectory is the asymmetric architecture of the molecule as measured by $\boldsymbol{R} = \sum_i(\lambda_i \boldsymbol{r}_i)/\lambda$ in Eq. (3). For a symmetric molecule such as a sphere, $R = 0$. According to Eq. (9), there is no net mean displacement as would be expected.

As Eq. (11) is derived from Langevin equation, environmental parameters such as temperature and solvent density are implicit in the damping coefficient and random terms. The spiral patterns of the trajectories are statistically averaged. The time dependent term $T(t)$ in Eq. (11) stands for the relaxation of the inertia. Environmental parameters such as temperature and solvent density could influence the damping coefficient and make the formation of spiral patterns become faster or slower.

3. Molecular dynamics simulation

We have performed molecular dynamics (MD) simulation to demonstrate the spiral trajectories. MD simulation, in which the trajectories of atoms and molecules are determined by numerically solving Newton's equations of motion for a system of interacting particles, has been widely accepted as a powerful tool for studying the dynamics of molecules at nanoscales.[30–32] In the simulation model, we design a model molecule composed of six atoms bonded into a regular hexagonal shape with the side length of 0.2 nm, as sketched in Fig. 1(e). All six atoms have the same van der Waals interaction parameter and same radius ($\sigma = 0.375$ nm, $\varepsilon = 0.439$ kJ·mol^{-1}). Only one atom has seven times the mass of the others. The lighter atoms have the mass of $m = 8$ u and the heavier atoms have the mass of $m = 56$ u. From Eq. (3), we can obtain $R = 0.1$ nm for this asymmetric molecule. The simulation system consists of 2500 model molecules moving freely in a 2D box of dimensions 40 nm×40 nm with periodic boundary conditions, as shown in Fig. 1(e). The cut-off distance for van der Waals interactions was set to 1.3 nm. There was no Coulomb interaction in this system. A time step of 1 fs was used, and the neighbor list was updated every ten steps. The temperature was maintained at 300 K by a Nose–Hoover thermostat[33,34] using Gromacs 2016 software.[35] The simulation was run for 12 ns and the last 10 ns were collected for analysis.

As shown in Figs. 1(a)–1(d), the spiral patterns in the mean trajectories can be clearly seen. We emphasize that the mean trajectories from MD simulations here are in excellent agreement with the theoretical analysis we obtained above. The simulation data were binned according to θ_0 that denotes the samples falling in the range $[\theta_0 - \Delta\theta_0, \theta_0 + \Delta\theta_0]$ and ω_0 that denotes the samples falling in the range $[\omega_0 - \Delta\omega_0, \omega_0 + \Delta\omega_0]$. We used $\Delta\theta_0 = 0.1\pi$ and $\Delta\omega_0 = 1$ rad/ps. The average runs over the segments of trajectories of all model molecules in the simulation box. The length of segment used here is 10 ps.

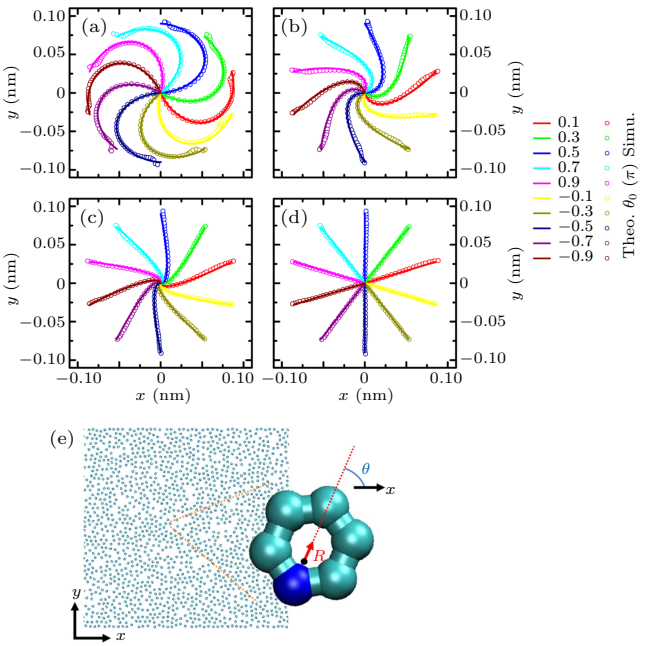


Fig. 1. (a)–(d) Typical mean trajectories predicted by Eq. (10) (lines) for an asymmetric molecule with $R = 0.1$ nm for different initial orientation angles θ_0 (from -0.9π to 0.9π) and different initial angular velocities $\omega_0 = 2.0$ rad/ps (a), 0.8 rad/ps (b), 0.3 rad/ps (c) and 0 (d), respectively. The symbols are the MD simulation data. (e) Snapshot of the simulation system and sketch of a model asymmetric molecule, where the blue sphere represents the heavy atom, and the black point denotes the CoM of the molecule. The red arrow represents the vector $\boldsymbol{R}$ defined in Eq. (3) and θ is the angle between $\boldsymbol{R}$ and the x-axis.

4. Conclusion

To summarize, spiral patterns are observed in the mean trajectories of asymmetric molecules down to the length scale of only several Angstroms by solving the under-damped Langevin equations. The existence of the spiral trajectories has also been demonstrated by molecular dynamics simulation. We believe that this is the first observation of the spiral patterns in the systems down to molecular length scale of only several Angstroms. The key to the spiral motion lies in the asymmetric architecture of the molecules that leads to a translation–rotation coupling. This unexpected dynamic behavior has a similarity to that of active matters. In fact, in our previous work, we have shown a non-zero resultant force originating from the imbalanced collisions on an asymmetric nanoparticle.[36] We note that this spiral motion only happens in finite time before the onset of random diffusive regime since it solely results from thermal fluctuations without any input of

external energy. Thus, it will not lead to a perpetuum mobile that violates the second law of thermodynamics. This is similar to the spontaneous unidirectional rotations of the triptycene in the molecule designed by Kelly *et al.* that were observed over a short time period,[37] where "the second law survives".[38] Moreover, if we average the trajectories over the initial orientation θ with equal probability in all directions, the effects of spiral trajectories disappear and the averaged result follows the diffusive regime of Brownian motion, which is consistent with principles of statistical mechanics.

Considering that a majority of physical, chemical and biological processes happen on the nanoscale within finite time and most of the involved molecules possess asymmetric structures, we expect that the spiral trajectory we discovered here may have considerable influence on the understanding of various processes at the molecular level. For example, intracellular signaling is usually carried out by small signal molecules over a distance of several nanometers to their receptors on a finite timescale.[39–41] Further, the spiral pattern in molecular motions may be of great help to the bottom-up understanding of the molecular mechanism in some special fluid phenomena, like vortices. However, how to evaluate the role of spiral motion in the dynamics of these processes remains to be an open and challenging research subject.

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