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Brownian dynamics of self-regulated particles with additional degrees of freedom: Symmetry breaking and homochirality

Debankur Bhattacharyya,[1] Shibashis Paul,[2] Shyamolina Ghosh,[2,*] and Deb Shankar Ray[2,†]
[1]*Indian Institute of Technology Kharagpur, Kharagpur, West Bengal 721302, India*
[2]*Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India*

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We consider the Brownian motion of a collection of particles each with an additional degree of freedom. The degree of freedom of a particle (or, in general, a molecule) can assume distinct values corresponding to certain states or conformations. The time evolution of the additional degree of freedom of a particle is guided by those of its neighbors as well as the temperature of the system. We show that the local averaging over these degrees of freedom results in emergence of a collective order in the dynamics in the form of selection or dominance of one of the isomers leading to a symmetry-broken state. Our statistical model captures the basic features of homochirality, e.g., autocatalysis and chiral inhibition.

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I. INTRODUCTION

Collective behavior of a system of interacting particles resulting in fascinating phenomena of self-organization has been an interesting domain of study in physical sciences [1–4] since the mid-1990s. This has greatly influenced our understanding of bird flocks [5], fish schools [6], animal herds [7], insect swarms [8], bacterial suspensions [9], migrating ants [8], movement of crowds [10], etc., in diverse apparently disjoint fields. The collective coherent behavior observed over a wide range of spatiotemporal length scales, sometimes referred to as "flocking" has been investigated experimentally both in living and nonliving systems [11–15]. Attempts have been made to construct minimal models to understand several basic features of phase behavior and universality of the underlying self-propelled dynamics [1,3,16,17].

A major characteristics of the self-propelled behavior of particles is that the system remains under far from equilibrium condition. One observes nonequilibrium transition between the ordered (flocked) state and the disordered state in presence of an optimal strength of external noise on the particles which move at discrete time steps with constant speed and align with the neighbors within an intermediate range of radius that serves as the interaction length scale of the particles. The physics of the equilibrium phase transitions in classical theory has been fruitfully employed to here capture several aspects of nonequilibrium transition and the associated symmetry breaking [1–5,17–19]. The purpose of this paper is to search for collective behavior of a system of self-regulated Brownian particles in the state of thermal equilibrium. This self-regulation is determined by the additional degree of freedom of each particle which corresponds to its state. For example, if a molecule exists in three states or forms corresponding to two isomers (or enantiomers) [+1] and [−1] and an intermediate [0] (racemic or achiral state), then there are three values of this degree of freedom of the molecule(in general, particle). Thus each moving particle is characterized by its position coordinate, momentum, and an additional degree of freedom. The time evolution of the particle coordinate and momentum is governed by the usual Brownian dynamics in a bath at a fixed temperature. However, at each instant the dynamics of the additional degree of freedom of a particle is guided by the local average of the same of its neighbors within an optimum radius of interaction. Two conspicuous features of the scheme distinct from the models of self-propelled dynamics [1,16–19] and active Brownian motion [3,20–24] are noteworthy. First, the dynamics of the phase-space coordinates, i.e., position and momentum of the particle is not directly influenced by the time evolution of the additional degree of freedom. But the time evolution of the degree of freedom of a particle at any time at a spatial location is determined by those of its neighbors whose spatial locations depend on the Brownian dynamics of the particles. Second, since in the case of self-propelled dynamics the particles exchange energy with an external source, the system remains in a far-from-equilibrium condition. The Brownian dynamics of the particles considered here is thermally equilibrated, implying that the detailed balance and fluctuation-dissipation relation are strictly obeyed in the entire description. Temperature has a special role to play, as it controls the transition rates between the different states of the additional degree of freedom. In what follows we consider the collective dynamics of a system of Brownian particles each with an additional degree of freedom which can assume three distinct states, [0], [+1], and [−1]. We show that when one starts from an achiral, symmetric state, the time evolution of the additional degrees of freedom of the particles guided by their local averages and the thermal condition determining the transitions between the states leads to a symmetry-broken state, i.e., a state in which one of isomers (or enantiomers) overwhelmingly dominates over the other. To characterize this transition behavior we introduce the notion of an order

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[*] Present address: University of Kansas, 1450 Jayhawk Blvd, Lawrence, KS 66045, USA.

[†] Corresponding author: pcdsr@iacs.res.in

parameter in terms of this degree of freedom rather than in terms of magnitude of the average momentum of the particles, which is a measure of nonzero flow in the ordered phase. Our approach to the symmetry breaking of a state under thermal equilibrium thus provides a clue to the search for a homochiral state from a racemic mixture or achiral state. We examine this issue in the perspective of Frank model [25] for homochirality realized as a symmetry-breaking phenomenon under far-from-equilibrium conditions in a nonlinear dynamical system and of the later experimental developments.

Finally, a pertinent point needs to be mentioned. The dynamics considered here is quite distinct from the population dynamics in a cellular automaton [26] where the particles do not move from the cells but evolve in time as per stochastic interaction rules. That the cells participate in Brownian motion is an essential element of the present theory since the stochastic transition between the states of the degree of freedom depend on local averaging as well as temperature of the thermal bath. As the temperature is lowered significantly the particles tend to remain in their own cells in absence of thermal diffusion and thermal transitions between the states are strongly hindered, resulting in an achiral state or a racemic mixture. This is irrespective of how long we run the simulations. Furthermore, temperature plays a crucial role in controlling the diffusion of order parameter. Finally, we also mention an interesting connection of stochastic interaction rules to the voters model [27]. In this model, a voter at each point on a connected graph interacts with its neighbors. The opinion of a voter on some issue may change randomly under the influences of the opinions of its neighbors. Since the opinion of a voter may take values like 0, 1, or ±1, 0, one can think of a close connection of this sequential dynamical system to our model, although there is no analogue of thermal transition.

The paper is organized as follows: In Sec. II we introduce the model and discuss the salient features of the Brownian dynamics of self-regulated particles with additional degrees of freedom at equilibrium. Section III is devoted to the results and discussions centering on the aspects of symmetry breaking and homochirality. The paper is concluded in Sec. IV.

II. BROWNIAN DYNAMICS OF PARTICLES WITH ADDITIONAL DEGREE OF FREEDOM

A. Theoretical formulation

The model consists of N particles distributed over a two-dimensional area of sides L. The state of each particle (say ith) is characterized by the vector $[x_i(t),y_i(t),v_{x_i}(t),v_{y_i}(t),\sigma_i(t)]^T$ at time t, where x_i, y_i are the position components and $v_{x_i}(t)$, $v_{y_i}(t)$ are the corresponding velocity components and $\sigma_i(t)$ denotes the internal degree of freedom of the ith particle. Depending on the nature of the underlying model σ_i may assume different values. For the present problem σ_i can take only discrete values $+1, 0, -1$. To be specific, we consider the three values to correspond to three different forms or states of a chemical species. $\sigma = 0$ corresponds to its metastable intermediate state while $+1$ and -1 are the two distinct stable states (or two isomers or enantiomers). The metastable state is relatively higher in energy than the two stable isoenergetic states by an amount ΔE which does not depend on the actual state of the system. The interconversion of forms of the chemical species between two stable states is only allowed via the metastable state.

The time evolution of position and velocity coordinates in two dimensions is guided by the Langevin equations for the particles,

$$\dot{x}_i = v_{x_i}, \tag{2.1}$$

$$\dot{v}_{x_i} = -\gamma_i v_{x_i} + F_i(t), \tag{2.2}$$

and the similar equations for $\dot{y}_i$ and $\dot{v}_{y_i}$, where index i runs from 1 to N and γ_i is the corresponding friction coefficient. $F_i(t)$ is a Gaussian, white noise with zero mean and correlation given by

$$\langle F_i(t)\rangle = 0 \quad \langle F_i(t)F_i(t')\rangle = \gamma_i kT\delta(t-t'). \tag{2.3}$$

The particles are thermalized at a temperature T. For the sake of simplicity we assume that there is no cross correlation between the noise and $\gamma_i = \gamma$ for all the particles. The use of a single γ facilitates the condition for attainment of equilibrium since, at equilibrium, temperature T is related to γ through the strength of the thermal noise D as $T = \frac{D}{\gamma}$, with k unity.

Now at any instant of time, the time evolution of σ_i is guided by the following consideration. We assume that the interactions between the particles are short ranged. Let r_i be the radius within which the ith particle can interact with its neighbors and change its state of internal degree of freedom σ_i depending on the average of the internal degree of freedom of its neighbors within this r_i. Let the region covered by the radius r_i be denoted by U_i and N_{U_i} is the number of particles within U_i. We define the average $\langle\sigma_i(t)\rangle_{U_i}$ as follows:

$$\langle\sigma_i(t)\rangle_{U_i} = \frac{1}{N_{U_i}}\sum_{j\in U_i}\sigma_j(t). \tag{2.4}$$

The state of ith particle $\sigma_i(t)$ evolves with time according to the following rules:

$$\sigma_i(t+\Delta t) = \begin{cases} 0 \text{ with } P = \exp[\frac{-\Delta E}{kT}], & \text{if } \sigma_i(t) = +1 \text{ or } -1 \\ \begin{cases} 1\times \operatorname{sgn}\langle\sigma_i(t)\rangle_{U_i}, & \text{if } \langle\sigma_i(t)\rangle_{U_i} \neq 0 \\ 0, & \text{if } \langle\sigma_i(t)\rangle_{U_i} = 0 \end{cases} & \text{if } \sigma_i(t) = 0 \end{cases}. \tag{2.5}$$

The system is equivalent to a chemical system in which two isoenergetic isomers ([+1] and [−1]) are in equilibrium with the intermediate species [0]. The above scheme shows that the intermediate [0] is produced from [+1] and [−1] isomers with probability $P = \exp\frac{-\Delta E}{kT}$, where ΔE accounts for the activation barrier for the formation of the intermediate from [+1] or [−1] species. The activation barrier for the formation of intermediate [0] is the same for both species [+1] and [−1].

Thus both [+1] and [−1] species are equally likely to be converted to the intermediate [0]. The intermediate [0] can transform into [+1] or [−1] species only via nonzero local averaging of σ as shown in (2.5). If the local average is 0, then the particle continues to remain as the intermediate. It is thus evident from Eq. (2.5) that local averaging over the states of the degrees of freedom of the neighbors as well as the temperature of the thermal bath determine the time evolution of the degree of freedom of the particles.

A further clarification on the nature of the system at equilibrium described by Eqs. (2.1)–(2.5) seems pertinent. While the system is in thermal equilibrium it is necessary to distinguish the Brownian dynamics that governs the displacement of particles from the chemical reaction. The first is a thermodynamically closed system and is independent of the third degree of freedom σ, which is in equilibrium. However, the chemical reaction which involves the passage of particles from the achiral state [0] to [±1] states is controlled by local inhomogeneity which drives the reaction towards a specific population type implies an inherent nonequilibrium nature of the reaction process. More specifically, the chiral inhibitory steps of the reaction are controlled by equilibrium thermal transitions; the autocatalytic conversion of the achiral molecules to chiral species entails typical local nonequilibrium transitions reminiscent of the features of active systems, where the orientational order parameter is "diffused" through the system by displacement of particles so that a local chiral order can autoenhance the transition to a more chiral state.

B. Symmetry breaking and approach to homochirality

The above stochastic three-state scheme can be explored in the perspective of Frank model of homochirality [25] proposed more than half a century ago. The model is based on a simple idea that a chiral chemical species can act as an autocatalyst for its self production. This autocatalysis which gives rise to amplification of the species is accompanied by chiral inhibition when the chiral species and its enantiomer combine to give an achiral compound or a racemic mixture. If the two chiral enantiomers are denoted by D and L and the achiral species by A, then the scheme according to the model is

$$\text{auto catalysis}\begin{cases} A+D \xrightarrow{k_D} 2D \\ A+L \xrightarrow{k_L} 2L \end{cases}$$

$$\text{chiral inhibition}\left\{ D+L \xrightarrow{k} 2A, \right. \tag{2.6}$$

where k_D, k_L, and k are the rate constants for the corresponding processes. A chiral enantiomeric excess defined as $\theta = \frac{[D]-[L]}{[D]+[L]}$, where $[D]$ and $[L]$ are concentration of the D and L forms, evolves in time as

$$\frac{d\theta}{dt} = \frac{1}{2}k([D]+[L])\theta(1-\theta^2). \tag{2.7}$$

Of the three fixed points $\theta = 0$ is unstable while ±1 are the stable homochiral fixed points. It follows simply from the dynamics that starting from any point in the D-L plane (i.e., any mixture) the system converges to one of the homochiral fixed point.

In the context of the present three-state scheme we now consider [+1] and [−1] states to correspond to D and L forms of enantiomers while [0] state refers to the achiral species. Since the molecules in state [0] undergo conversion to molecules in [+1] or [−1] forms depending on the excess number of the neighbors of 0 species, more +1 forms are produced from the 0 form when there are more +1 species as neighbors and, similarly, −1 forms are produced when more −1 species are present as neighbors. This enhancement of population of one form relative to other is basically an autocatalytic amplification and corresponds to first two autocatalytic steps of the Frank model. On the other hand, the passage of [+1] and [−1] forms of molecules to [0] form, the achiral state mimics the chiral inhibition. In our case the [+1] and [−1] molecules independently go over to the [0] state due to thermal transitions. This is similar to the case considered by Jafarpour *et al.* [28].

Although the present scheme does not make any explicit reference to autocatalytic kinetics and is stochastic in nature, it captures the basic features of homochirality (i.e., autocatalysis and chiral inhibition) regardless of the specific details of the underlying models. The model shows that each of the chiral species ([+1] or [−1] forms) or enantiomers can reproduce itself in a reaction with an achiral substrate ([0] form) through autocatalysis and, further, they can deactivate themselves to loose their capacity to self-reproduction through chiral inhibition. With the experimental proof of the concept behind the Frank model in the work of Soai and coworkers [28,29], who reported autocatalytic alkylation of pyrimidyl aldehydes with dialkylzines in which the reaction is accelerated by the catalytic amount of its alcohol product, it was realized that chiral molecules of alcohols, amino acids, hydrocarbons, organic crystals, and also heterogeneous chiral materials can act as chiral triggers for asymmetric autocatalysis.

In spite of the parallelism between the Frank model and the present one in terms of the key features of the homochirality or enantiomeric excess there are two essential differences. First, the Frank model is a nonlinear dynamical model while the present scheme is based on a stochastic approach. Second, the Frank model deals with a thermodynamically open system under far-from-equilibrium conditions. On the other hand, we consider here the diffusive Brownian dynamics at thermal equilibrium which relies on the fluctuation-dissipation relation. It is the local averaging effect that leads to symmetry breaking in the global system.

For characterization of the statistical properties of the system, it is convenient to introduce an order parameter which is the magnitude of the absolute value of the average of the internal degree of freedom (σ_i) as

$$\phi = \frac{1}{N}\left|\sum_{i=1}^{N}\sigma_i\right|. \tag{2.8}$$

Usually reactions that give rise to two different isomers (enantiomers) from an intermediate (racemic or achiral compound) lead to formation of two isomers (enantiomers) in equal proportions and the overall system remains unbiased or homogeneous. The nonzero value of ϕ is a measure of the domination of population of one isomer (or enantiomer) over the other and can be identified as isomeric excess. ϕ vanishes for a perfect achiral mixture of two isomers (or racemic mixture) for a large system, while the order parameter ϕ close to unity corresponds to a state of broken symmetry, i.e., a state with excess population of one of the isomeric forms, i.e., the homochiral state.

C. Three-state model and master equation

In order to understand the role of spatial resolution in the three-state scheme, we first consider the interaction circle to be equal to the extensions of the considered box. Our object here is to look for stationary properties of system for a comparison with spatially resolved numerical investigation as carried out in the next section. The loss and gain of populations of the three states can be described by the following master equation:

$$\frac{dP(s_j,t)}{dt} = -\sum_i W_{ji} P(s_j,t) + \sum_i W_{ij} P(s_j,t), \quad (2.9)$$

where $P(s_j,t)$ is the probability of finding the particle in the s_jth state ($s_j = +1,0,-1$) and W_{nm} is the transition probability per unit time for the transition from $n \rightarrow m$ state and given by

$$\begin{aligned} W_{-1,0} &= W_{+1,0} = Ae^{-\frac{\Delta E}{kT}} = \lambda(T) \\ W_{0,-1} &= \frac{1}{N}(N_- - N_+), \quad N_- > N_+ \qquad (2.10) \\ \text{and} \quad W_{0,+1} &= \frac{1}{N}(N_+ - N_-), \quad N_+ > N_-, \end{aligned}$$

where λ is the rate constant with a preexponential frequency factor A. The three state master equations for $\frac{dP(0,t)}{dt}$, $\frac{dP(+1,t)}{dt}$, and $\frac{dP(-1,t)}{dt}$ can be solved subject to the initial condition $P(0,0) = P_0 = 0$; $P(+1,0) = P_{+1} = P(-1,0) = P_{-1} = \frac{1}{2}$ and the constraint $P(0,t) + P(-1,t) + P(+1,t) = 1$ to obtain $P(0,t) = 1 - e^{-\lambda t}$ so that in the stationary limit $P(0,\infty) = 1$. This implies that starting from a racemic mixture of equal proportion of enantiomers of $+1$ and -1 states one reaches the achiral zero state. Thus there is no scope for any situation that leads to homochirality.

One may also approach a little variant of the problem from a purely kinetic consideration as follows:

$$\begin{aligned} \dot{n}_0 &= k_1 n_+ + k_2 n_- + k_0(n_0 - n_+)n_0 + k_0(n_0 - n_-)n_0 \\ \dot{n}_+ &= -k_1 n_+ - k_0(n_0 - n_+)n_0 \qquad (2.11) \\ \dot{n}_- &= -k_2 n_- - k_0(n_0 - n_-)n_0, \end{aligned}$$

where n_0, n_+, and n_- are the populations of isomers in 0, $+1$, and -1 states of σ, respectively, and k_0, k_1, and k_2 are temperature-dependent rate constants. The nonlinear terms indicate that large population of n_+ or n_- will increase n_+ and n_-, respectively, at the cost of n_0. The model is purely dynamical and conservative so that $n_0 + n_+ + n_- = c$, a constant. Elimination of n_0 from the equation yields

$$\begin{aligned} \dot{n}_+ &= (k_0 c - k_1 - k_0 n_+ - k_0 n_-)n_+ - k_0(c - n_+ - n_-)^2 \\ \dot{n}_- &= (k_0 c - k_2 - k_0 n_+ - k_0 n_-)n_- - k_0(c - n_+ - n_-)^2. \end{aligned} \quad (2.12)$$

At the stationary state, $\dot{n}_+ = \dot{n}_- = 0$. This gives

$$\begin{aligned} (k_0 c - k_1 - k_0 n^s_+ - k_0 n^s_-)n^s_+ &= k_0(c - n^s_+ - n^s_-)^2 \\ (k_0 c - k_2 - k_0 n^s_+ - k_0 n^s_-)n^s_- &= k_0(c - n^s_+ - n^s_-)^2, \end{aligned} \quad (2.13)$$

where the superscript "s" denotes the stationary population. For the isoenergetic [+1] and [−1] states $k_1 = k_2$. This results in

$$n^s_+ = n^s_-. \quad (2.14)$$

Equality of population of the two isomers clearly indicates that in the long-time limit the system returns to a racemic mixture or achiral configuration irrespective of the starting mixture, i.e., a state of broken symmetry is not achieved. Thus local averaging is an important element for causing symmetry breaking which can be captured only by spatially resolved dynamics.

Before leaving the section it is interesting to point out that Eq. (2.12) is reminiscent of the dynamics of competitive species [30], particularly competitive Lotka-Voltera models, where each species has one term for self-interaction and one term for interaction with others in addition to linear growth term. Such self-interaction terms like n_+^2, n_-^2 and other interactive terms like $n_+ n_-$ are immediately apparent in Eq. (2.12).

III. NUMERICAL SIMULATIONS: SYMMETRY BREAKING AND HOMOCHIRALITY

We have seen that a three-state model without spatial resolution cannot give rise to any asymmetry in the population distribution of the two isomers. This rules out the possibility of homochirality for any specific population type. We therefore proceed to explore the spatially resolved dynamics of the molecules undergoing Brownian motion. The motion of Brownian particles with their additional degrees of freedom is simulated numerically [31,32] by generating Gaussian noise using Box-Muller algorithm. The time evolution is followed in discrete time steps with the following parameter set for a system with $N = 4000$ and $L = 1000$; $\Delta E = 50$, $D = 0.1$, and $\gamma = 0.01$. Here D is the strength of noise and L is the length of a square box. The equilibrated system is characterized by a temperature $T = \frac{D}{\gamma} = 10$ with Boltzmann constant set equal to unity. We employ periodic boundary condition and minimum image convention throughout our simulation work.

We consider a system of racemic mixture, i.e., a system of particles in all three states of σ_i with the ratio

$$[\sigma = +1] : [\sigma = -1] : [\sigma = 0] = m : m : (1 - 2m) \quad (3.1)$$

set as the initial condition for the dynamics, m being a number between zero and unity and the populations are of the order of one thousand. The state of the ith particle, $\sigma_i(t)$ evolves with time following the rules of the scheme (2.5) with local averaging of σ_i in a circle of radius r_i and dynamical equations (2.1)–(2.3) for x_i and v_{x_i} and corresponding equations for y_i and v_{y_i}. We assume further that $r_i = r$, i.e, the radius of interaction is same for all particles. Assigning different r_i for different particles does not influence the dynamics qualitatively. Monitoring mean-square velocity $\langle v^2 \rangle$ until it converges to $\frac{2D}{\gamma}$ has been done to check the attainment of equilibrium of the system.

The results of our numerical simulations are presented in Figs. 1–6. In Fig. 1 we exhibit the variation of population fractions of three species with time for the above-mentioned parameter values and radius $r = 10.0$. The population fraction of intermediate [0] is controlled by the Boltzmann factor

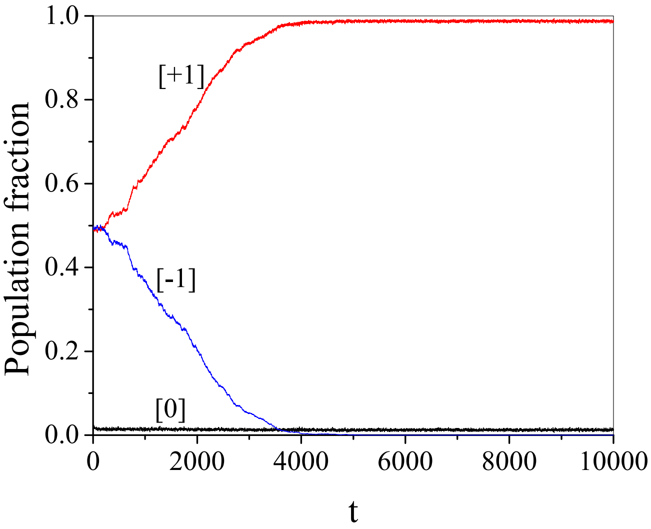

FIG. 1. Plot of population fraction vs. time t for [+1], [−1], and [0] species for $N = 4000$, $L = 1000$, $r = 10.0$, $\Delta E = 50$, $m = 0.5$, $D = 0.1$, $\gamma = 0.01$, and $\Delta t = 1$ (units arbitrary).

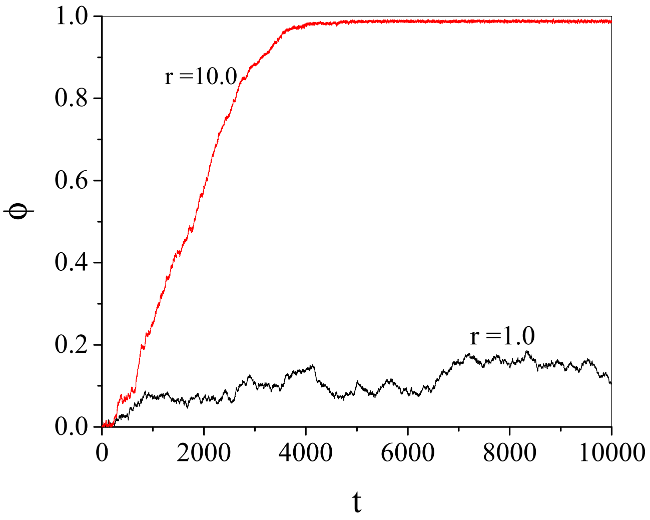

FIG. 2. Plot of order parameter ϕ vs. time t for the system with $N = 4000$, $L = 1000$, $\Delta E = 50$, $m = 0.5$, $D = 0.1$, $\gamma = 0.01$, and $\Delta t = 1$ for two different values of r. $r = 1$ leads to an almost symmetric state while $r = 10$ results in symmetry breaking (units arbitrary).

$\exp[\frac{-\Delta E}{kT}]$. It is apparent from Fig. 1 that the overall symmetry of the system in terms of population of [+1] and [−1] species breaks down with progress of time. All the [−1] species are converted to [+1] and once the system reaches equilibrium there are only [+1] species in large proportion and [0] species in minuscule proportion in the system. The relative ratio of [+1] and [0] species is controlled by the back reaction probability $P = \exp[\frac{-\Delta E}{kT}]$. The choice that only the species [+1] prevails after the attainment of equilibrium is arbitrary. In different runs of the simulation, [−1] species may also appear as the dominant species. That one of two isomers or enantiomers dominate in large proportions imply that the global state is a state of broken symmetry due to local averaging.

The magnitude of order parameter ϕ represents the overall bias of the system towards the population of a single isomer or enantiomer. In Fig. 2, ϕ is plotted against time for two different values of radius r, which may be treated as an effective length scale of autocatalysis. Around $r = 1$ the local averaging effect fails to induce any bias to any specific form of isomer over a timescale of $t = 10\,000$. But for $r = 10.0$, one observes a clear bias of the system towards one isomer (enantiomer). In other words, the system with no initial bias undergoes symmetry breaking in the long time limit. It has been checked that on further lowering of the effective radius of interaction r less than $r = 1$, statistical fluctuations become too limited, and the particles are thermally excited so that all the [+1] and [−1] species are converted to [0] species with equal probability and the system goes over an unbiased or racemic state or symmetric configuration.

The dependence of the order parameter ϕ on the effective radius of interaction r averaged over last 1000 time steps has been depicted in Fig. 3. It is apparent from the plot that ϕ remains close to zero for low values of r but increases rapidly with r along with large fluctuations. The fluctuations tend to settle down at large r. The fluctuations can be reduced by carrying out average over multiple data sets as shown in Fig. 3(b). We point out an apparent contradiction of Fig. 3(b) with our conclusion from Sec. II C where it was shown through an analytical scheme that at an interaction radius spanning the whole box one would get a racemic mixture. The contradiction can be resolved once we take care of diffusion in the spatial model, which is not considered in the model of Sec. II C. The spatial diffusion is an integral part of the Brownian dynamics which in turn affects the order parameter through the interaction rules. This diffusion of order parameter, in fact, seems to be more important than the interaction size.

In the study of emergence of coordinated motion like bacterial swarms, bird flocking etc, the main control parameter in the noise-induced symmetry breaking under far from equilibrium condition is the strength of the external noise. Since in the present system we consider a thermally equilibrated condition which ensures validity of the fluctuation-dissipation relation, it is likely that temperature can be chosen to serve as a control parameter for the study of symmetry breaking. To this end, we consider the variation of order parameter as a function of time for several values of temperature (D) in Fig. 4 and for two different ensembles corresponding to equal population (a) of [+1] and [−1] species and with a population distribution (b) 25% in [+1] and 25% in [−1] states and 50% in the [0] state. As the temperature of the system determines the population of [0] species, we observe that at very low temperature ($D = 0.06$) the population of the intermediate remains unaffected and the order parameter remains almost close to zero in long-time limit. With gradual rise of temperature from $D = 0.06$ to 0.10, we observe a distinct bias towards a specific population type, resulting in symmetry breaking at a faster rate. This is regardless of any initial achiral ensemble.

Figure 5 depicts the variation of order parameter as a function of temperature D with averaging over last 1000 time steps for different runs of simulations. With large fluctuations in the

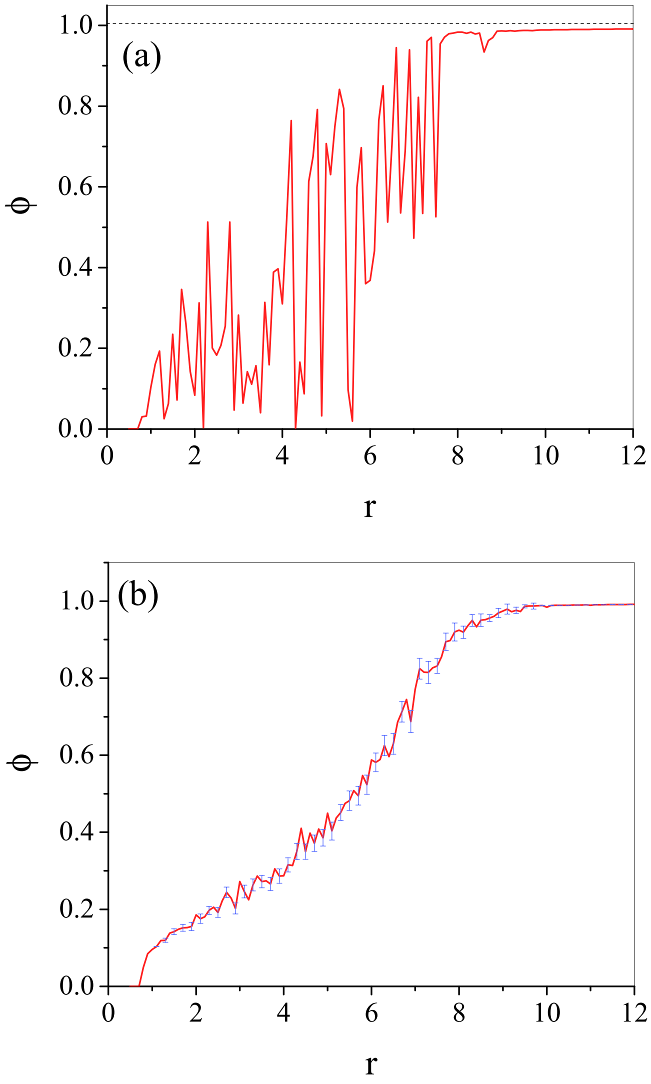

FIG. 3. Plots of variation of the order parameter as a function of effective radius of interaction r for a system with $N = 4000$, $L = 1000$, $\Delta E = 50$, $m = 0.5$, $D = 0.1$, $\gamma = 0.01$, and $\Delta t = 1$. For each run of simulation with a fixed value of r, order parameter is calculated by taking time average over last 1000 time steps. (a) Plot for a single scan over different values of r. (b) Plot for averaged over 100 data sets for 100 different scans over r with error bars (units arbitrary).

intermediate range, the variation shows a distinct transition from an unbiased state ($\phi \approx 0$) to a state of broken symmetry ($\phi \approx 1$). The noise can be smoothed out to a large extent by taking average over multiple data sets as shown in Fig. 5(b). The curve shows a distinct sigmoid type trend characteristic of a phase transformation. Furthermore, for a relatively higher rise in temperature D, we observe a slight decreasing trend in ϕ. The plausible reason is that at higher temperature the population of the [0] species increases, as a result the isomeric excess decreases with a slight lowering of ϕ.

Finally, we note that in the present model the decay reaction is controlled by the temperature of the system, i.e., the decay is fueled by the kinetic energy of the whole system. This leads to an "entanglement" between the Brownian dynamics and the decay rate of the chiral molecules to the achiral state.

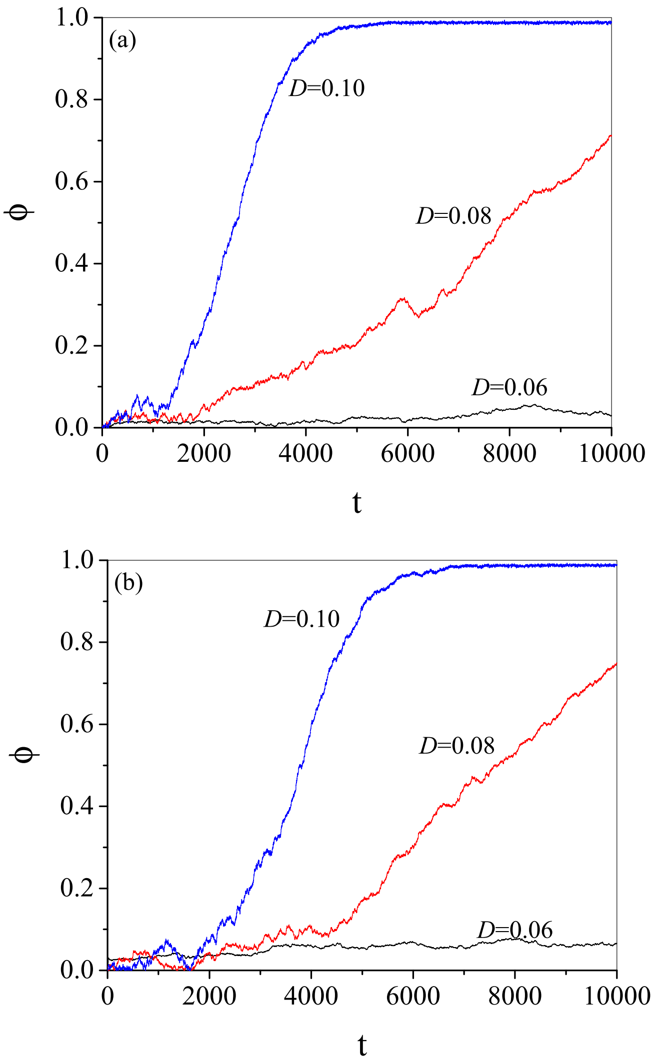

FIG. 4. The variation of order parameter ϕ with time t for several values of temperature D for two sets of initial populations with $N = 4000$, $L = 1000$, $r = 10.0$, $\Delta E = 50$, $\gamma = 0.01$, and $\Delta t = 1$ (a) $m = 0.5$; (b) $m = 0.25$ (units arbitrary).

While the effect of temperature is to enhance the decay rate of the chiral molecules, another crucial role of temperature is to induce spatial diffusion whose strength is quantified by γkT, i.e., the strength of the thermal noise. In other words thermally induced diffusive transport results in a nonzero order parameter through spontaneous symmetry breaking. To throw more light into this aspect we have studied the variation of order parameter with activation energy ΔE to distinguish between the effect of chiral molecular decay and the effect of spatial diffusion of the order parameter at a fixed temperature in Figs. 6(a) and 6(b). With large fluctuations in the intermediate region, the variation of order parameter as a function of ΔE exhibits a sigmoidal transition curve from the $\phi = 1$ to $\phi = 0$ state [Fig. 6(a)]. As in the previous case the fluctuations are smoothed out after averaging aver 100 data sets [Fig. 6(b)]. For relatively higher values of ΔE the decay of chiral molecules is strongly hindered. Low activation barrier, on the other hand, promotes strong chiral inhibition. The spatial diffusion of the

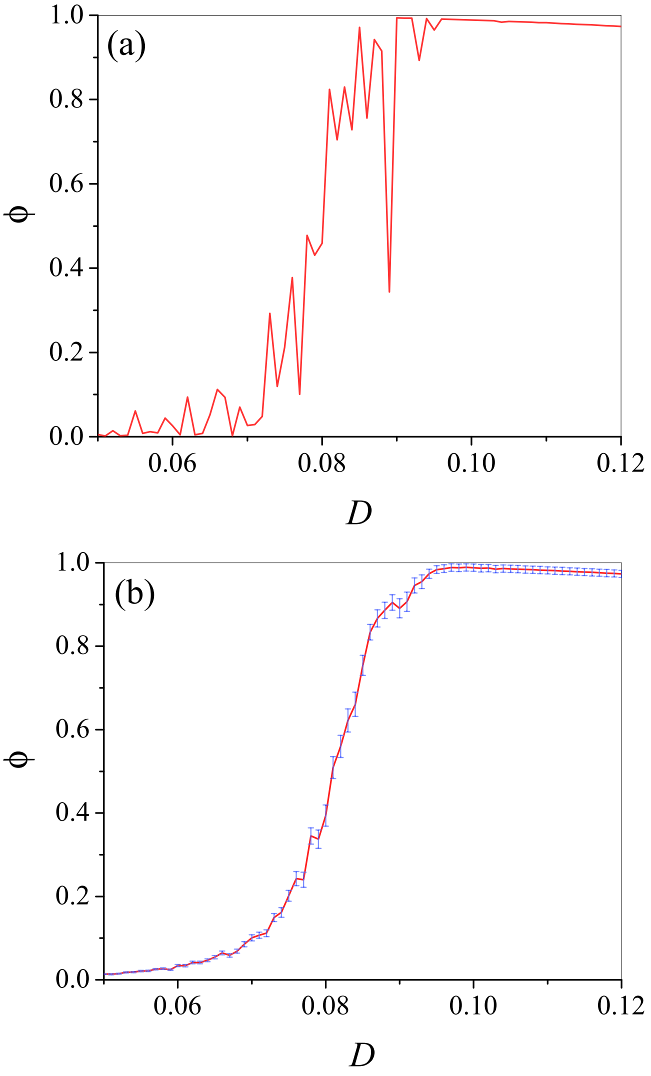

FIG. 5. Variation of order parameter ϕ with temperature D for $N = 4000$, $L = 1000$, $\Delta E = 50$, $m = 0.5$, $r = 10.0$, $\gamma = 0.01$, and $\Delta t = 1$ For each run of simulation with a fixed value of D the order parameter is averaged over last 1000 time steps. (a) Plot for a single scan over D. (b) Plot for average over 100 data sets with error bars for 100 different scans over D (units arbitrary).

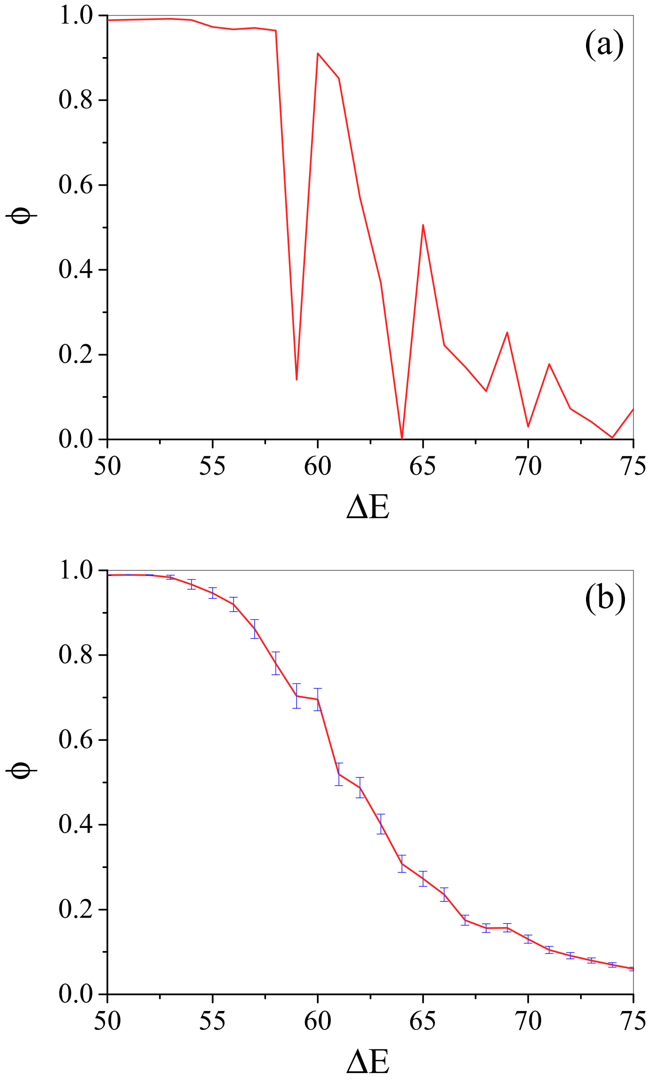

FIG. 6. Variation of order parameter ϕ with activation energy ΔE for $N = 4000$, $L = 1000$, $D = 0.1$, $m = 0.5$, $r = 10.0$, $\gamma = 0.01$, and $\Delta t = 1$ For each run of simulation with a fixed value of ΔE the activation energy is averaged over last 1000 time steps. (a) Plot for a single scan over ΔE. (b) Plot for average over 100 data sets with error bars for 100 different scans over ΔE (units arbitrary).

order parameter, on the other hand, is independent of ΔE but is controlled by thermal noise strength γkT.

The nonmonotonic dependence of order parameter on temperature is a consequence of the stochastic interaction rules (2.5). At a finite temperature the particles in the stable states [+1], [−1] make transitions to unstable state [0] with equal probability. When the temperature is too low, this probability becomes very small and the particles in the stable state tend to remain there resulting in an order parameter close to zero. At a higher temperature the transition probability gets larger and a significant population of particles in the unstable state builds up. This is accompanied by transition of particle from the unstable state [0] to any of the two stable states when majority of the particles surrounding this particle inside the interaction radius are in that state. A local enhancement of population in one of the stable states (which are fed from the unstable state with a significant population) brings in asymmetry of the population of the particles in the two stale states giving rise to homochiral stationary state.

IV. CONCLUSIONS

In this paper we have investigated the ensembles of Brownian particles each with an additional degree of freedom. The additional degree of freedom can assume three values corresponding to three states standing for the two stable isoenergetic isomers being separated from an unstable third state. The coordinates and momenta of the particles are governed by the associated Langevin equations. The time evolution of the additional degree of freedom is discrete and depends on two factors. First, depending on the thermal condition, i.e., temperature the unstable [0] state gets thermally populated from the two isoenergetic states [±1] with Arrhenius probability. Second, the reverse transitions, i.e., the passage of isomers from [0] state to the [±1] states depends on their neighbors. The ensemble interaction rules are such that the unstable state is left in favor of the two stable states if the majority of the particles surrounding of this particle inside a ring around are in one of these states. Otherwise, the states are left in favor of the unstable one by thermal agitation. Since the positions of the particles in the immediate neighborhood are determined by the Langevin dynamics of the system thermalized at a given temperature, Brownian motion remains an essential element in the present theory. Thus the Brownian motion of the particles is not affected by the degree of freedom of the particles, but the evolution of the degree of freedom depends on the Brownian motion which controls the temperature and the position of the particles. We now summarize the main conclusions of this study.

First, our proposed three-state model and the stochastic interaction rules show that starting from a symmetric, achiral population distribution of the three isomers, local averaging and thermal transition lead to the selection of one of the isomers resulting in a collective order and symmetry breaking of the system. Nowhere in the present theory we have included any explicit chiral bias. An order parameter has been associated to describe the symmetry breaking.

Second, since the transitions from the two stable states are thermal in nature, we have shown that temperature helps reaching a symmetry-broken state at a faster rate. This is irrespective of the relative initial populations of the states of the ensembles or achiral mixtures. The variation of order parameter with temperature characterizes this symmetry-breaking transition.

Third, we have shown that as the enhancement of population of one of the two isomers depends on the excess population of that isomer in its close neighborhood, the enhancement is an autocatalytic nonequilibrium step, while the thermal transitions from the two enantiomeric states mimic the chiral inhibitory steps. These two steps are the essential components of a theory of homochirality as supported by experiments on asymmetric synthesis. Our model thus effectively incorporates these prime features of homochirality.

Fourth, while the majority of the models of homochirality are primarily based on nonlinear dynamics under far-from-equilibrium condition, the present approach to homochirality is statistical in nature and relies on thermal condition. Both statistical fluctuations and equilibrium condition are closely corroborated by experiments on amplification of enantiomeric excess in a chemical reaction.

Finally, we mention that, depending on the specificity of the situation, it is possible to generalize and/or to entend the scheme for two-state or multistate models with appropriate modification of the stochastic interaction rules. For interacting species models in ecology, thermal condition in addition to stochastic rules may play an important role since various infections are promoted by optimal temperature. For a voters model, on the other hand, thermal transition rules are to be replaced by appropriate alternative stochastic rules.

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