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Microphase Separation of Semiflexible Ring Diblock Copolymers

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Electronic Supplementary Information

Abstract Aiming at the difficult problem of solving the conformation statistics of complex polymers, this study presents a novel and concise conformation statistics theoretical approach based on Monte Carlo and Neural Network method. This method offers a new research idea for investigating the conformation statistics of complex polymers, characterized by its simplicity and practicality. It can be applied to more complex topological structure, more higher degree of freedom polymer systems with higher dimensions, theory research on dynamic self-consistent field theory and polymer field theory, as well as the analysis of scattering experimental data. The conformation statistics of complex polymers determine the structure and response properties of the system. Using the new method proposed in this study, taking the semiflexible ring diblock copolymer as an example, Monte Carlo simulation is used to sample this ring conformation to construct the dataset of polymer. The structure factor describing conformation statistics are expressed as continuous functions of structure parameters by neural network supervised learning. This is the innovation of this work. As an application, the structure factors represented by neural networks were introduced into the random phase approximation theory to study the microphase separation of semiflexible ring diblock copolymers. The influence of the ring's topological properties on the phase transition behavior was pointed out.

Keywords Ring copolymer; Diblock copolymers; Semiflexible; The order-disorder transition

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INTRODUCTION

The theoretical research and experimental synthesis of cyclic polymers have attracted wide attention. Recently, the influence of cyclic topological structures in self-assembly has been explored. In earlier studies, Marko calculated that the interlayer spacing of cyclic polymers could be reduced to 0.63 of that of linear analogues.[1] This was later confirmed by Lecommandoux and colleagues.[2] Subsequently, Poelma *et al*. achieved smaller interdomain spacing, as low as 19.5 nm, compared to linear analogues, through the self-assembly of cyclic block copolymer PS_{13000}-*b*-PEO_{5000} in thin films.[3] This confirmed the use of cyclic topology in nanolithography to produce smaller and faster nanoelectronic devices compared to conventional methods. Furthermore, research on topological dynamics and conformational has been highly regarded. Particularly, after the groundbreaking work by Kapnistos *et al*.,[4] who used Monte Carlo (MC) technique to investigate the conformational and dynamic properties of polymer rings and ring-linear blends. Lee and Jung used lattice space Monte Carlo simulation to study the slow diffusion process in polymer ring melts and its relation to the topological constraints imposed by interpenetration of different ring molecules.[5] Reigh and Yoon employed lattice Monte Carlo simulations to examine the effect of concentration on the conformational of cyclic polymers.[6] Shanbhag,[7] Henke and Shanbhag[8] utilized a bond fluctuation model in their Monte Carlo simulations to investigate the dynamic properties and conformational properties of symmetric and asymmetric ring-linear copolymer blends. The structure factor for cyclic systems is typically obtained through the basic mathematical formula of density-density correlation function.[1,9–12] Herschberg[13] compared the ordered-disordered transition (ODT) process in melts of symmetric linear, cyclic and trefoil knots diblock copolymers with the same chain length using coarse-grained molecular dynamics simulations, emphasizing the importance of the chain topology in influencing the microphase separation of block copolymers. Marko employed the random phase approximation (RPA) theory to determine that the phase transition point for linear copolymers occurs at $\chi N = 10.5$.[1] Qian and Lu *et al*. applied the dissipative particle dynamics (DPD) simulation method to study the mesoscopic phase formation of cyclic diblock copolymer c-A_mB_n. The phase diagram is constructed by simulating at different interaction parameters and composition fractions. The resulted phase diagram is similar to that of the linear diblock copolymer; *i.e*., the ordered structures such as lamellae, perforated lamellae, hexagonal cylinders, and body-centered-cubic spheres can be identified in the parameter space.[14] Qiang and Li *et al*. developed an accelerated pseudospectral algorithm for self-consistent field theory (SCFT) of ring copolymers using

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the "combination symmetry" of propagators, which directly reduces the number of diffusion equations to be solved.[15] They constructed phase diagrams of AB ring copolymers and AB tadpole copolymers using numerical techniques such as cuFFT callbacks and batch processing computations. Kim *et al*. first established the SCFT structure of Gaussian ring polymers, enabling the prediction of equilibrium nanostructures in topologically unconstrained ring polymer systems.[16] They successfully discovered phase separation in ring homopolymer blends and ring diblock copolymer melts. Ryu *et al*. modeled rigidness-variable diblock and double-arm graft copolymers using coarse-grained molecular dynamics, demonstrating that graft copolymers are more suitable than diblock copolymers as compatibilizers for immiscible homopolymer blends.[17] In terms of experimental synthesis, the main technique currently used are bimolecular ring closure, unimolecular ring closure, and ring expansion technique. Notably, the introduction of "click" chemistry,[18] which offers highly efficient, mild, and selective reactions, has brought about significant technological innovations. Clever application of the self-accelerating "click" reaction in bimolecular ring closure greatly enhances the rate of cyclization reactions, minimizing the formation of low polymers.[19,20] This method has also been employed to generate hyperbranched multi-ring polymers.

In summary, the influence of cyclic topology on the dynamics and conformational properties of cyclic polymers, compared to linear polymers, has been extensively studied, including diffusion behavior, crystallization kinetics, rheology, *etc*.[16,21–25] In recent years, there has been an increasing number of simulation or modeling studies, providing suitable polymer samples for experimental validation, stimulating further experimental research to synthesize new functional polymers. In terms of material synthesis, new approaches have been developed to study the effects of cyclic topology by utilizing adaptive polymer materials that respond to photon, thermal, electronic, or chemical stimuli under non-equilibrium conditions.[26–30] Additionally, in the field of biomedical applications, the topological effects of cyclic polymers have been employed to achieve enhanced biotransport and gene or DNA delivery, among others.[31–34]

It should be noted that cyclic polymers generally have relatively low degrees of polymerization, and their rigidity cannot be ignored. Moreover, in the synthesis of multifunctional polymers, the properties of the system are often controlled by designing the topology, chain rigidity, and block structures. The emergence of these novel and complex polymer structures has increased the complexity of the theory. The structure and responsive properties of complex polymer systems are determined by polymer conformation statistics, with the structure factor serving as a physical quantity that can describe conformation statistics. However, for semiflexible ring polymers, solving the diffusion equation for conformation statistics is extremely challenged, and there are currently no relevant theoretical reports. Therefore, for solving conformation statistics problems in complex polymer systems, this study proposes a novel and concise Monte Carlo and Neural Network theoretical approach, as shown in Fig. 1, which is the innovation of this study.

Taking the microphase separation of semiflexible ring diblock copolymers as an example, this study demonstrates the theoretical advantages of the proposed method in dealing with complex polymer conformation statistics. Firstly, a target model is designed. Monte Carlo methods are used to simulate semiflexible ring diblock copolymers and sample their conformation. The structure factor, along with associated physical quantities such as rigidity coefficients and wavenumber, which can describe conformation statistics, are discretized to form a training dataset. A fully connected neural network is used to fit and train the dataset, obtaining the neural network representation of the structure factor for this copolymer. Numerically, it serves as a two-dimensional continuous function of polymer rigidity coefficient and wavenumber. As an application, the neural network representation of the structure factor is incorporated into the random-phase approximation theory to study the microphase separation in semiflexible ring diblock copolymers and calculate their ordered-disordered transition points.

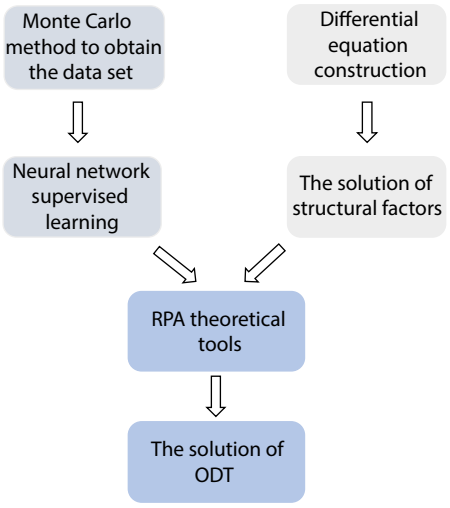

Fig. 1 Method comparison chart. On the left is the comparison between the conformational statistical method presented by the neural network and the traditional method of solving structure factors on the right.

THEORY AND METHOD

The structure and response properties of polymer systems are determined by their conformation statistics. Experimentally, by designing the topology of the polymer chain, the composition of the block and the rigidity of the molecular chain, the conformation statistics of the polymer can be controlled. Especially in recent years, the successful synthesis of ring polymers has broken through the linear topology of traditional polymers with ends. Meanwhile, since the degree of polymerization of ring polymers is relatively low, their rigidity should not be ignored. In fact, due to the introduction of topological constraints, it has become very difficult to solve equations, so the theoretical research of not only ring polymers, but also various polymers with complex topological structures is in a state of stagnation.

Therefore, taking semiflexible ring diblock copolymers as an example, the study applies the Monte Carlo and neural network this new model to solve its structure factors and characterize the conformation statistics of polymers, and then

deeply understand the properties and behavior of polymers, so as to provide theoretical support and guidance for the design and application of polymers.

From the perspective of rigidity, ring copolymers can be divided into Gaussian ring copolymers, rigid ring copolymers and semiflexible ring copolymers. Under different rigidity, the presentation state is different. As shown in Fig. 2, Fig. 2(a) is a Gaussian cyclic diblock copolymer, Fig. 2(b) is a semiflexible cyclic diblock copolymer, and Fig. 2(c) is a rigid cyclic diblock copolymer. The biggest difference can be observed as the difference in the local chain bending potential energy.

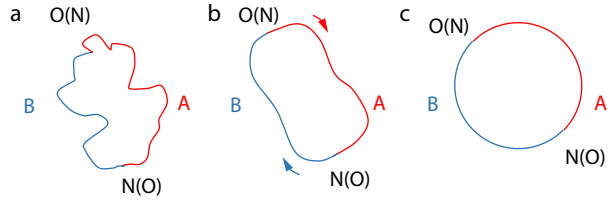

Fig. 2 Diagram of ring diblock copolymers with different rigidities: (a) Gaussian diblock copolymers, (b) semiflexible diblock copolymers, and (c) rigid diblock copolymers.

The energy of the system is composed of bond angle energy and bond energy. The Gaussian ring model is constrained by bond energy when the local chain is stretched, but does not take into account the bending potential energy, that is, the constraint of the bond angle energy, when the chain is bent. The relationship between bending potential energy (bond angle energy) and polymer ring rigidity can be achieved through the calculation of the potential energy function

$$U_{\text{bend}} = \sum_{i=2}^{N-1} V_{\text{b}}(\vartheta_i) \tag{1}$$

Suppose ϑ_i is the bond angle formed by the three monomers of i–1, i, i+1, and $V_{\text{b}}(\vartheta_i)$ is the bond angle energy, written as

$$V_{\text{b}}(\vartheta_i) = k_{\text{b}}[1 - \cos(\vartheta_i)] \tag{2}$$

where k_{b} is the rigidity coefficient. When k_{b} is 0, the polymer chain is completely flexible. When k_{b}<<1, the polymer chain is completely rigid. According to McLaurin's formula, bond angle energy can be approximately expressed as:

$$V_{\text{b}}(\vartheta_i) \approx \frac{k_{\text{b}}}{2}\vartheta_i^2 \tag{3}$$

The rigidity of the ring copolymer can be changed by changing the rigidity coefficient k_{b}. This allows the model to encompass the full scale range from flexible to rigid. With the change of the rigidity factor k_{b}, the rigidity of the cyclic copolymer can be also changed. This allows the model to cover a full scale range from flexibility to rigidity.

In this work, the simplest monocyclic topology is adopted, and by the linear diblock copolymer head and tail again block, form a circular diblock copolymer. When constructing this model, it can be seen that the linear copolymer A and B interact, and the beginning point O of component A is defined as the same position as the end point N of component B, and similarly, the end point N of component A is defined at the same location as the end start point O of component B. In this way, cyclic diblock copolymers are formed. The schematic diagram is shown in Fig. 2(b).

The semiflexible cyclic diblock copolymer in this work is composed of AB two components, where the A component profile length is L_{A}, the B component profile length is L_{B}, the total length is $L = L_{\text{A}} + L_{\text{B}}$. The volume fraction of component A is $f = L_{\text{A}}/L$. In this work, the chain length L is set to 100, and the contour lengths of both A and B components are 50, so the cyclic copolymer has a symmetrical structure.

In order to overcome the computational difficulty of obtaining structure factors by numerical solution of modified diffusion equations, this paper proposes a research scheme to construct neural network representations of structure factors from data. Here, we take the semiflexible cyclic diblock copolymer, which is a typical problem that is difficult to solve by traditional numerical values, as the object, and show a new research scheme to obtain the structure factor that can describe conformational statistical information under any rigidity coefficients, that is, the conformational statistical method of Monte Carlo-Neural Network. Firstly, the Monte Carlo method is used to sample the conformational of the polymer in equilibrium to obtain the simulation data of the structure factors that can characterize the conformation statistics. And then the neural network is used to perform supervised learning on this dataset, by adjusting the structural parameters of the neural network, the structure factors represented by the neural network are finally obtained.

For model of cyclic diblock copolymers for semiflexibleity, given the volume fraction f and rigidity coefficient k_{b} of component A, the Monte Carlo method is used to sample the polymer conformational in equilibrium and solve the structure factors. The construction of the dataset is completed, the volume fraction f, the wavenumber k and the rigidity coefficient k_b are taken as the input parameters, and the structure factor is used as the output parameters. In order to explore the influence of different rigidity on structure factor, multiple rigidity coefficients are set in this paper. The Monte Carlo method simulates semiflexible ring polymers at each rigidity coefficient.

The first is the initial setup of the semiflexible chain. In MC simulations, ring polymers are discretized into a series of ring chains with the same bond length in continuous space. The thermodynamic equilibrium state of the semiflexible cyclic diblock copolymer is reached by thermal relaxation by Monte Carlo simulation. The second step is to simulate the conformation changes of the copolymer, and sample it. The Monte Carlo simulation in this paper mainly uses the Metropolis sampling algorithm. The details are as follows:

The energy of the polymer chain is E_i and the probability of P_i state i is:

$$P_i \sim \exp\left(-\frac{E_i}{k_{\text{B}}T}\right) \tag{4}$$

where k_{B} is the Boltzmann constant. In the Metropolis sampling algorithm, the probability of transition from a high-energy state to a low-energy state is

$$P_{i\to j} = 1, E_j \le E_i \tag{5}$$

Acceptance probability of transition from low-energy to high-energy state is calculated as follows:

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$$P_{i\to j} = \exp\left(-\frac{E_j - E_i}{k_B T}\right), E_j > E_i \quad (6)$$

The Monte Carlo sampling algorithm for semiflexible ring copolymer conformation is as follows:

(1) Randomly select a monomer i on the polymer chain and get the energy U_{old} of the polymer chain;

(2) Give the monomer i a random displacement $\Delta\boldsymbol{r}$: $\boldsymbol{r}_i = \boldsymbol{r}_i + \Delta\boldsymbol{r}$ to generate an attempted conformation, corresponding to the energy of U_{new};

(3) Calculate the energy difference before and after the attempt to move: $\Delta E = U_{new} - U_{old}$;

(4) According to equation (6), determine whether to try to move. If so, accept this attempt to move, and then update the system conformation and as the initial conformation of the next attempt to move; if not, the attempt will not be accepted and go back to the first step to reselect a new monomer to try to move.

Structure factor is then calculated. Each time the system conformation is updated, each component corresponding to a structure factor, and by definition, the structure factor of the semiflexible ring diblock copolymer is:

$$S(\boldsymbol{k}) = \frac{1}{L}\sum_{n,m}\left\langle \frac{\sin(|\boldsymbol{k}|\,|\boldsymbol{r}_n - \boldsymbol{r}_m|)}{|\boldsymbol{k}|\,|\boldsymbol{r}_n - \boldsymbol{r}_m|}\right\rangle \quad (7)$$

where, L is the chain length, $\boldsymbol{k}$ is the wave vector, $\boldsymbol{r}_i$ is the position vector of the i^{th} polymer segment in free space, and m, n are the free metering variables of the segment.

For the repeated simulation to find its average, in order to reduce the time cost and improve the computational efficiency, for each cyclic diblock copolymer with rigidity coefficient, 10 parallel calculations of different initial conformations are carried out, and the structure factors under each rigidity coefficient are derived from the algebraic mean of 10 parallel calculations.

The relevant parameters of Monte Carlo simulation method are set as follows: the number of parallel chain chains is 10, the chain length is 100, the number of segments of A and B components is 50, the average key length is 0, and the average fluctuation of bond length is 1. For each rigidity coefficient k_b, the wavenumber k ranges from 0.1 to 2 takes 50 values, sets 2×10^4 Monte Carlo simulations, that is, 2×10^5 independent conformations to calculate the structure factors of each component.

Monte Carlo method is used to obtain independent conformations of semiflexible ring diblock copolymers, in order to solve the structure factors of each component and build the training dataset of neural network. The dataset is used as the drive for adequate fitting training. This paper aims to obtain the continuous function of structure factors on rigidity coefficients and other parameters through supervised learning of neural networks, so as to obtain structure factors under any relevant parameters. Replace the cumbersome process of solving complex differential equations in traditional methods.

Before training the model, it is necessary, to initialize parameters. The weight parameters of the model are randomly sampled from a normal distribution with a mean of 0 and a standard deviation of 0.01. In this work, the activation function used is the ReLU function:

$$f(x) = \text{relu}(x) = \max(x, 0) \quad (8)$$

Mini-batch stochastic gradient descent (sgd) with learning rate a of 0.02 is specified as the optimization algorithm, and each mini-batch is set to 10 samples. This algorithm is used to iterate over all parameters contained in all layers nested by the add function in the net instance, which can be obtained by the collect_params function. Through neural network experiments with different number of layers and measured by loss function value and time cost, it proves that four-layer fully connected neural network is the most appropriate neural network structure. For details, please refer to the electronic supplementary information (ESI). Therefore, this neural network is applied in the following, and the neurons of each layer are set to 1000, 1000, 12 and 1, respectively. In most neural network learning models, there is no analytical solution, and the corresponding solution can be obtained by optimizing the algorithm to reduce the value of loss function as much as possible after finite number of iterations of parameters.

The supervised learning process of neural networks, that is, by adjusting the weight parameter w to gradually learn the mapping relationship from input to output. Define a loss function:

$$\text{Loss}(\boldsymbol{w}) = \frac{1}{N}\sum_x \|f(x) - h_{\boldsymbol{w}}(x)\|^2 \quad (9)$$

It represents the distance of the function h from the objective function f. For semiflexible cyclic diblock copolymers, the training task can be described as $x_j = (f_j, k_{bj}, k_j)^T$ and $y = f(x)$ =structure factor C_{aa} of component A, structure factor C_{bb} of component B, and structure factor C_{ab} of component A-B, as shown in Fig. 3, which is the structure of the fully connected neural network mainly used in this study.

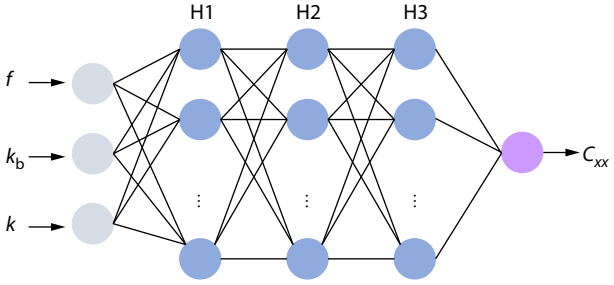

Fig. 3 This work mainly uses four-layers of fully connected neural network.

The purpose of supervised learning using neural networks is to train and fit discrete Monte Carlo simulation datasets at specified scales, so there is no overfitting problem in this paper. In other words, by supervising the learning of the rigidity coefficient and the mapping relationship between the wavenumber and the structure factor, the continuous function of the structure factor to the wavenumber k can be obtained under the given discrete rigidity coefficient k_b. At the same time, a two-dimensional continuous function of structure factors to rigidity coefficient k_b and wavenumber k can also be obtained. Thus, any structure factor within the specified scale range is obtained, that is, the final aim is to obtain the continuous function of the structure factor to the rigidity coefficient and wavenumber.

The theoretical method of random phase approximation (RPA) is an important tool for solving the microscopic phase

separation of polymer systems, and its core is to solve the reciprocal of the architectural factor, that is, the association function $C_{RPA}(\boldsymbol{k})$, the association function $C_{RPA}(\boldsymbol{k})$ can be calculated by:

$$C_{RPA}^{-1}(\boldsymbol{k}) \equiv \frac{\Sigma(\boldsymbol{k})}{C(\boldsymbol{k})\Sigma(\boldsymbol{k}) - \Delta^2(\boldsymbol{k})} - \frac{\chi N}{2} \tag{10}$$

in which

$$\begin{aligned} C(\boldsymbol{k}) &\equiv C_{AA}(\boldsymbol{k}) - 2C_{AB}(\boldsymbol{k}) + C_{BB}(\boldsymbol{k}) \\ \Delta(\boldsymbol{k}) &\equiv C_{AA}(\boldsymbol{k}) - C_{BB}(\boldsymbol{k}) \end{aligned} \tag{11}$$

$$\Sigma(\boldsymbol{k}) \equiv C_{AA}(\boldsymbol{k}) + 2C_{AB}(\boldsymbol{k}) + C_{BB}(\boldsymbol{k}) \tag{12}$$

where the core part of this analysis is the calculation of structure factors. This can be done by traditional calculation of the density-density pair correlation function of the ring chain model. However, in this paper, the structure factor of the semiflexible cyclic copolymer is obtained through the new theoretical method of Monte Carlo and Neural Network, so that the structure factor of the system can be given in the numerical calculation program instead of the analytical form of the structure factor required by the traditional theory, and the structure factor of the system $C_{RPA}^{-1}(\boldsymbol{k})$ is given in the numerical calculation program. By finding the extreme values of the wavenumber, the stability limit of the cyclic diblock copolymer system can be determined, that is, the spinodal node χN of the ordered-disordered transition, and the wavenumber k^* of the most unstable fluctuation mode.

RESULTS AND DISCUSSION

Taking cyclic diblock copolymers as an example, we aim to obtain the structure factors C_{aa}, C_{bb}, and C_{ab} for each component of the copolymer at corresponding wavenumber, considering different rigidity. Since C_{aa}=C_{bb} always holds true due to symmetry considerations, in this study, we only focus on C_{aa}. As mentioned earlier, we uniformly select 50 different wavenumbers in the range of 10^{-1}–2×10^{0}, which covers the scale range required for further analysis of microphase separation instability using the RPA theory. For each specific rigidity of the cyclic diblock copolymer, we performed Monte Carlo simulations on ten polymer chains in parallel. After reaching thermal equilibration, we sampled each chain with 10^4 Monte Carlo steps to obtain a total of 10^5 independent conformations. By statistically averaging these independent conformations based on the definition of structure factors, we obtain the structure factors. Fig. 4 presents the structure factors C_{aa} and C_{ab} with wavenumber k as the x-axis. These figures plot the results for eight different rigidity coefficients. The solid lines represent the fitting results of the neural network (NN), while the solid dots represent the numerical values obtained from the Monte Carlo (MC) simulations. The rigidity coefficients k_b are taken as 0, 0.5, 1, 1.5, 2.5, 3.5, 5, and 10, represented by different colors in the figures. The use of unequal intervals is employed to reduce the number of MC calculations required. As shown in the figures, the structure factor obtained from the Monte Carlo simulations appears as a series of discrete data points at k values. However, in theory and experiments, the structure factor should be a continuous function of k and preferably a continuous function of the rigidity coefficient k_b as well. The neural network performs supervised learning on the

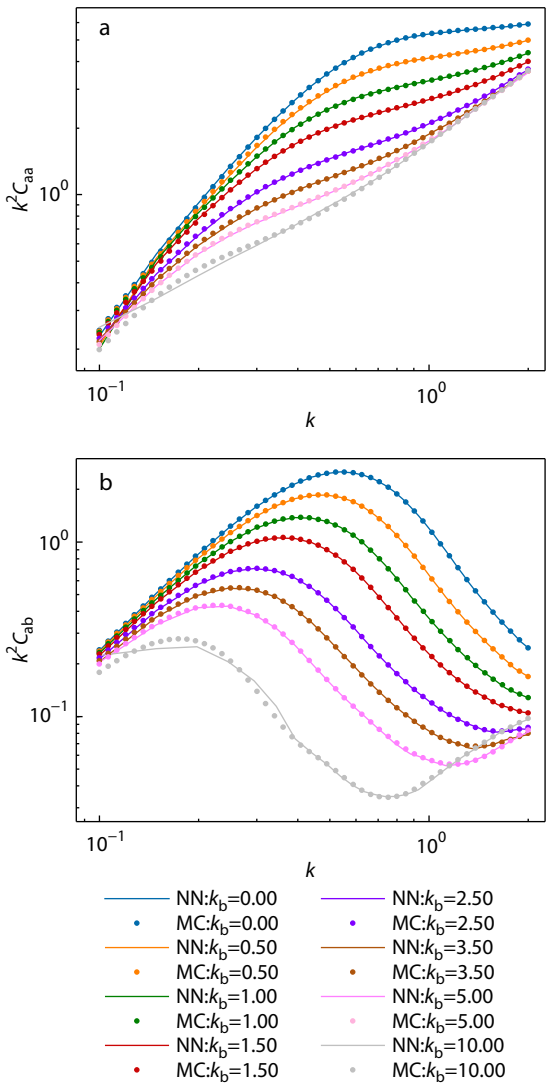

Fig. 4 The variation of structure factor with wavenumber for different rigidity coefficients k_b in a four-layer fully connected neural network. solid lines (NN) represent neural network fitting results, and solid dots (MC) represent Monte Carlo values. (a) Variation of the structure factor C_{aa} with wavenumber k. (b) Variation of structure factor C_{ab} with wavenumber k.

obtained Monte Carlo simulation dataset to obtain the functions $C_{aa}(k)$, $C_{ab}(k)$, $C_{aa}(k, k_b)$, and $C_{ab}(k, k_b)$.

For convenience, we adopt the Kratky diagram format commonly used in scattering experiments, where the vertical axis represents k^2C_{aa}, and both the horizontal and vertical axes are logarithmic. As shown in Fig. 4(a), with the same rigidity coefficient, the structure factor C_{aa} increases monotonically with the wavenumber k and goes through three characteristic scale regions: (I) the small k region, where k^2C_{aa}~k^2, is known as the Guinier region and reflects the scattering behavior of polymers at large scales. This region depends on the polymer's gyration radius; (II) the intermediate k region, corresponding to the mesoscopic scale, where the polymer's conformational exhibits random walks at this scale for high rigidity coefficients (*e.g.*, k_b=10). In this plot, it tends towards a horizontal line independent of k, *i.e.*, k^2C_{aa}~k^0. III. the large k re-

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gion, corresponding to small scales, where the polymer exhibits linearly connected chain behavior, *i.e.*, k^2~k^1. The exponent of k in each region (equal to d–2) depends on the fractal dimension d of the polymer chain at that scale. The turning points between these regions correspond to the macro-meso-micro boundaries. For polymers with different rigidity coefficients k_b, these transition points differ, and the stronger the rigidity, the smaller the corresponding k value of the transition point. With the same wavenumber k, as the rigidity coefficient k_b increases, the structure factor C_{aa} decreases successively.

The Kratky plot in Fig. 4(b) represents the structure factor C_{ab} between components A and B under Monte Carlo simulation, as a function of wavenumber k and the rigidity coefficient k_b. The dependence of C_{ab} on k is no longer monotonic for the same rigidity coefficient. As the wavenumber k increases, the structure factor C_{ab} first increases and then decreases. In the small k region, k^2C_{ab}~k^2, which still exhibits the characteristic behavior of Guinier and reflects the gyration radius of polymer. In the intermediate k region, it deviates from random walk behavior and exhibits novel oscillatory behavior arising from the cyclic conformational of the polymer, which is a key property of interest in this syudy. In the large k region, it still reflects the linearly connected chain behavior on a small scale, with k^2C_{ab}~k^1. This region can only be observed in a few cases with larger rigidity coefficients in the graph. In fact, if we expand the range of k of interest, the same phenomenon can also be observed for structure factors with smaller rigidity coefficients. Similar to the results of the structure factor between the same components, the transition point k in each region decreases as the rigidity coefficient increases. Overall, for the same wavenumber, the structure factor C_{ab} decreases as the rigidity coefficient increases.

The better the overlap between the solid line and the data points represented by the rings, *i.e.*, the more points observed on the line, the better the fitting effect. As indicated above, the solid rings and the solid line coincide well at macroscopic, mesoscopic, and microscopic scales, satisfying their scaling laws at individual scales. The fitted loss value reaches the order of magnitude of −6, which sufficiently demonstrates the high consistency between the fitted structure factor of the neural network and the simulated structure factor values from the Monte Carlo simulations in terms of rigidity and scale dependence. This also confirms that the Monte Carlo simulations employed in this paper can effective quantitatively reveal the conformational statistical properties of polymers at various rigidity and scales.

More importantly, the data obtained through Monte Carlo simulations consists of a limited number of discrete training samples in the $k_b - k$ parameter space, while the trained neural network model can provide a continuous function of structure factor across the entire parameter range. To demonstrate the characteristics of this continuous function, we plotted a heatmap of the structure factor C_{aa} in the continuous $k_b - k$ parameter space using the structure factor function represented by the neural network, as shown in Fig. 5(a). The horizontal axis represents the wavenumber k, the vertical axis represents the rigidity coefficient k_b, and the colors in the heatmap represent the values of k^2C_{aa}, with the color scale shown on the right side. Higher values are represented by colors closer to yellow-green, while lower values are closer to blue. It can be observed that, as k increases, k_b decreases and the value of k^2C_{aa} also increases. For the same wavenumber k, as k_b increases, the value of k^2C_{aa} decreases. For the same rigidity coefficient k_b, as the wavenumber k increases, the value of k^2C_{aa} increases. This is consistent with Fig. 4(a). Therefore, at the point where k is maximum and k_b is minimum in the graph, the value of k^2C_{aa} is maximum and the color is the brightest.

The heat map of the structure factor C_{ab} between components A and B is shown in Fig. 5(b). The horizontal axis represents the wavenumber k, and the vertical axis represents the rigidity coefficient k_b. The color in each region represents the value of k^2C_{ab}, as indicated by the color scale on the right side, where higher values are closer to yellow-green. In the graph, it can be observed that the maximum value of k^2C_{ab} corresponds to k between 0.3 and 0.6, with a corresponding k_b value of 0. For the same wavenumber, as k_b increases, the k^2C_{ab} value decreases. For the same rigidity coefficient, k_b, there exists a maximum C_{ab} value for each k, and the corresponding k value for the maximum k^2C_{ab} value decreases as k_b increases. This is represented in the graph by the trailing shadows in the upper left corner.

This method accomplishes the transformation from a dis-

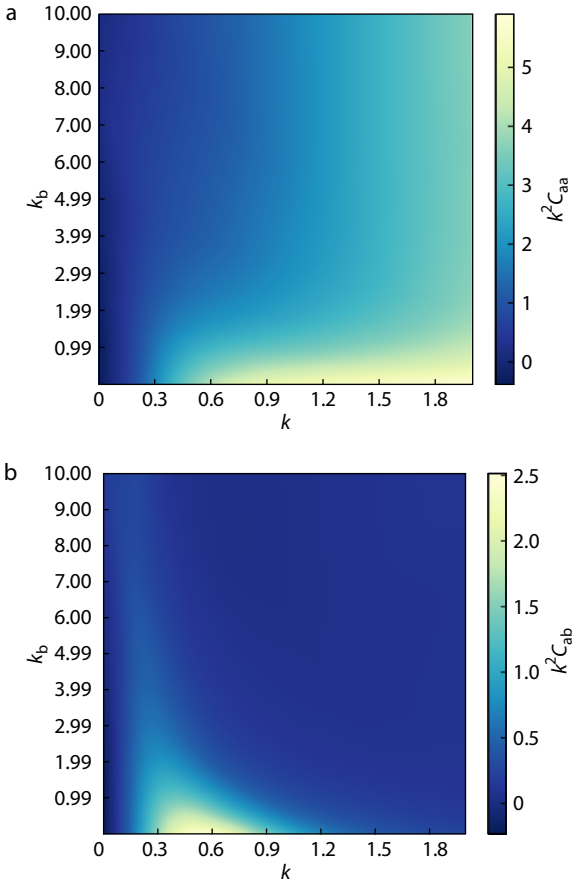

Fig. 5 The structure factor changes with wavenumber k and rigidity coefficient k_b. (a) Variation of the structure factor C_{aa}; (b) Variation of structure factor C_{ab}.

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crete small dataset to a two-dimensional continuous function model on the full rigidity-full length scale, extracting continuous conformation statistics of similar polymers from the statistical fitting of discrete single-chain conformations. The structure factor can be directly predicted for any pair of k and k_b. Furthermore, we can easily calculate the values of multiple structure factors simultaneously, thus eliminating the need for complex differential solving processes and greatly improving computational efficiency. Typically, the feasibility of this research requires that the function in the form of a neural network can only be applied within the range of k and k_b given by the simulated data or extended to neighboring regions. However, this requirement is not imposed in this paper. This is because the structure factor satisfies perfect scaling laws in both the small k and large k regions, independent of the data used in the training model. Additionally, for the rigidity parameters, they also exhibit perfect asymptotic properties as k_b approaches 0 and infinity, corresponding to the flexible and rigid limits, respectively. Therefore, the supervised learning approach used here does not suffer from extrapolation issues and is well-suited for the scientific problems addressed in this study.

According to the RPA theory, the structure factor of a system can be obtained from the single-chain structure factor $C_{RPA}^{-1}(\boldsymbol{k})$. In this work, we represent the structure factor of a semiflexible cyclic diblock copolymer as a continuous function of wavevector k using a neural network. This allows us to replace the traditional analytical form of the structure factor required in RPA theory and provide the system's structure factor $C_{RPA}^{-1}(\boldsymbol{k})$ in numerical calculations. By analyzing the extrema of the wavevector, we can determine the stability limit, characterized by the order-to-disorder transition wavevector χN, and the wavevector k^* corresponding to the most unstable fluctuation mode of the cyclic diblock copolymer system. For simplicity, we only consider symmetric diblock copolymers in which the two components, denoted as A and B, have the same chain length, and the volume fraction f of component A is set to 0.5. We define the quantity:

$$x \equiv \langle R_g^2 \rangle k^2 \tag{13}$$

to characterize the characteristic length scale of the microphase structure. Herein, $\langle R_g^2 \rangle = N/12$ represents the mean square radius of gyration and N is the degree of polymerization for the semiflexible cyclic diblock copolymer.

In this study, energy consumptions of different fluctuation modes x for various values of the rigidity coefficient k_b are obtained through neural network training. The energy consumption is characterized by χN. The numerical results are presented in Fig. 6 as a thermal map of $k_b - x$. The color legend on the right side represents the magnitude of χN, where the color gradually shifting towards yellow-green indicates larger χN values, while shifting towards blue indicates smaller χN values. As both the fluctuation modes and rigidity coefficient increase, it can be observed that the overall color changes from dark to light, with the presence of a deep blue band, indicating a decrease followed by an increase in χN values, forming a concave valley. When k_b is constant, as x increases, the χN values initially decrease and then increase. In other words, for a given rigidity of a polymer, there exists a

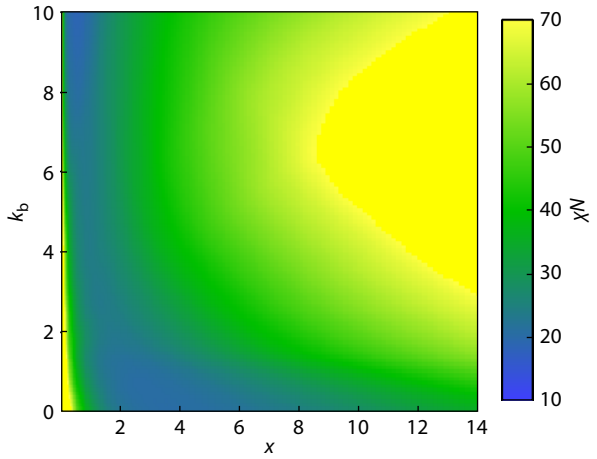

Fig. 6 The change of value of spinodal node χN with space size x, rigidity coefficient k_b.

minimum value of χN, referred to as the critical point or spinodal node. Its corresponding microphase structure characteristic scale is the length corresponding to the most unstable fluctuation mode x.

In order to observe the relationship between the spinodal node χN, the rigidity coefficient k_b, and the fluctuation mode x, we traverse the wavenumber to obtain the stable limits of the system. As shown in Fig. 7, the horizontal axis represents the rigidity coefficient k_b, the left vertical axis represents the spinodal node χN, and the right vertical axis represents the fluctuation mode x corresponding to the spinodal node χN. As the rigidity coefficient increases, the cyclic chain tends toward a circular shape, and the trend of the spinodal node χN first increases, as indicated by the green dashed line in the Fig. 7, indicating an expansion of the region of the disordered phase. Subsequently, the trend decreases, which implies an expansion of the stable region of the ordered phase. This corresponds to the color variation on the concave valley band in Fig. 6, where the ends are darker and the middle is relatively lighter. This can be explained as follows: in the ordered state, the Flory-Huggins repulsion χ between components A and B dominates and drives phase separation, while the chain conformational entropy decreases. With an increase in the rigidity coefficient, the conformational entropy increases, leading to a decrease in the region of the ordered phase and an increase in the region of the disordered phase. As the rigidity coefficient continues to increase, the conformational entropy decreases, resulting in an increase in the region of the ordered phase and a decrease in the region of the disordered phase. The fluctuation mode x corresponding to the spinodal node χN is shown as the blue dotted line in Fig. 7. As the rigidity of the cyclic chain increases, x exhibits a decreasing trend, consistent with the direction of the concave valley band in Fig. 6, which goes from the upper left corner to the lower right corner. For a given polymer system with a certain rigidity, when χN is higher than the spinodal node, the system is in ordered phase, indicating microscale phase separation. When χN is lower than the spinodal node, the system is in disordered phase. On a macroscopic level, the system's phase can be controlled by factors such as temperature and

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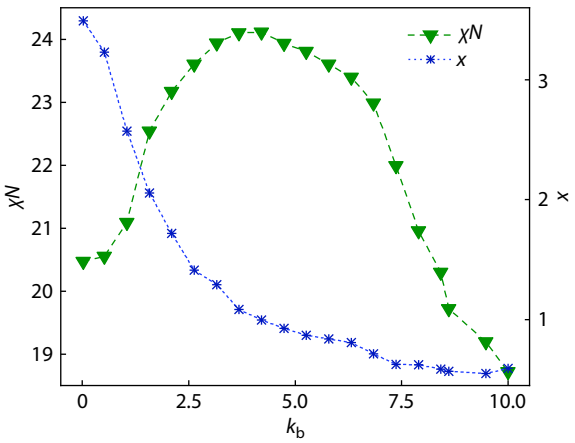

Fig. 7 The lowest spinodal node χN value (dotted green line) and its corresponding space size x (dotted blue line) change with the rigidity coefficient k_b.

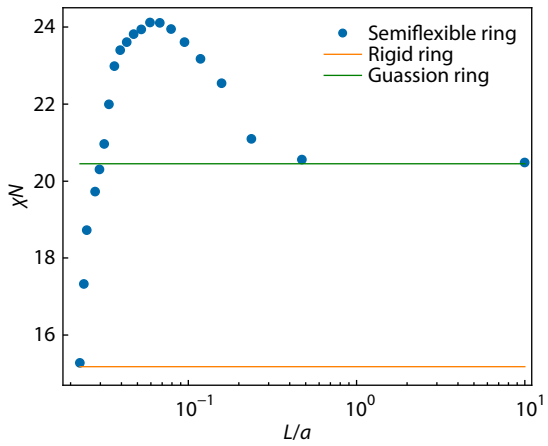

Fig. 8 The change of the lowest spinodal node χN value (blue dot) with different rigidity L/a, Gaussian ring spinodal node value (green solid line), rigid ring spinodal node value (orange solid line).

pressure, which affect the magnitude of χN.

Among various rigidity coefficients, the case of k_b=0 needs special attention as it represents the characteristics of a fully flexible chain, specifically a Gaussian diblock copolymer ring. As shown in Fig. 8, the vertical axis represents the spinodal node χN of the ring (blue dots), and the horizontal axis represents k_b normalized by L/a, with the relationship $k_b = a/(4L)$. It can be observed that the values of χN increase initially and then decrease as the rigidity increases. As indicated by the blue dots approaching the green solid line in Fig. 8, as L/a approaches the limit of complete flexibility, which corresponds to the spinodal node of a Gaussian diblock copolymer ring (green solid line). The spinodal node of the Gaussian diblock cyclic polymer calculated in the literature is reported to be 17.795, which differs from the value obtained in this work. The main reason for this discrepancy is the limitation of computational platform performance. The chain length used in this study is 100, which does not meet the theoretical requirements for flexible chains. However, the cost of conducting MC fitting for longer polymer chains is prohibitively high. However, under the rigid limit, it is theoretically expected that the circular chains should maintain a standard circular structure. This observation aligns with the phenomena we observed in the Monte Carlo experiments. Therefore, employing the method described in this work, the calculated value of the rotational node is consistent with the theoretical value, which is 15.177. This indicates that the Monte Carlo and Neural Network approach can enhance accuracy through parameter adjustments. As the rigidity further increases and k_b tends to infinity, when the horizontal axis approaches zero, the value of χN tends to the spinodal node of the corresponding rigid ring, as shown by the blue dots converging to the orange solid line in Fig. 8.

Particularly for the rigidity parameter, as k_b approaches zero and infinity, it can respectively return to the limits of flexibility and rigidity, exhibiting perfect asymptotic behavior. This fully describes the complete range of rigidity, encompassing the transitions from flexibility to semiflexibility and then to rigidity in the variation of the spinodal node of the ring, which is highly relevant to the semiflexible scientific problems addressed in this work.

CONCLUSIONS

This work proposes a novel theoretical method, the Monte Carlo-Neural Network conformation statistics model, to address the problem of solving conformation statistics for complex polymers. The innovation of this work lies in the introduction of the Monte Carlo and Neural Network approach. Using a multi-chain system of semiflexible cyclic diblock copolymers as an example, this study demonstrates the theoretical advantages of the Monte Carlo and Neural Network method in handling complex polymer conformation statistics.

The methodology firstly builds a model for the semiflexible ring diblock copolymer, setting the model parameters, and then perform Monte Carlo simulation to sample the conformational changes of the semiflexible diblock copolymer in space. This generates a discrete dataset for the ring diblock copolymer. By applying supervised learning technique of neural network, the discrete dataset is trained and fitted to obtain a two-dimensional continuous function representing the structure factor of the copolymer as a function of rigidity coefficient and wavenumber.

The results indicate that the structure factor within the same component exhibits linear dependence on rigidity and scale. Additionally, distinct from the behavior of linear random walks, the structure factor for different components displays significant oscillations due to their cyclic topological structure. This novel theoretical method can fit and compute the structure factor for any given combination of rigidity coefficient and wavenumber, and at the same time calculate multiple structure factors, thereby significantly enhancing computational efficiency. Normally, the feasibility of this research approach requires the neural network function to be applicable only within the range of k and k_b values provided by the simulation data or extended to neighboring k and k_b regions. However, in this study, no such restrictions apply because the structure factor satisfies perfect scaling behavior in both small k and large k regions, independent of the data used for model training. Additionally, the rigidity parameters exhibit perfect asymptotic properties as k_b approaches zero and infinity,

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corresponding to the limits of flexibility and rigidity, respectively. Hence, the supervised learning used here avoids the problem of extrapolation failure.

Finally, we present a representative application example of the structure factor expressed by neural network. We analyze the microphase separation phenomenon of semiflexible ring diblock copolymers. Using the structure factors of individual component obtained from the neural network as the basis of data, we employ the RPA theory to solve structure factor of the multi-chain system. This allows us to determine the order-disorder phase transition point of the microphase separated system. The obtained results depict a transition from the flexible chain limit to the rigid chain limit, providing a comprehensive view of the entire rigidity scale. Furthermore, we highlight the influence of cyclic topological characteristics, distinct from linear behaviours, on the phase behavior.

In conclusion, the novel theoretical method proposed in this work, the Monte Carlo and Neural Network model for conformation statistics, possesses the following characteristics: It allows for the straightforward acquisition of continuous structure factor values throughout the entire $k_b - k$ space, eliminating the need for complex mathematical modelling and overcoming the challenges of solving differential equations. Only a small number of data samples are required to fit the desired function for any relevant parameter. Compared with classical numerical calculation methods, the use of neural networks requires fewer experimental samples, can maintain the same computational accuracy, and is generally applicable to any polymer topology. It provides a new research approach for analysing the conformation statistics of complex polymer systems. This method can be attempted to be applied to polymers with more complex topological structures, such as ladder polymers and polymer networks. It can also be extended to higher degree of freedom polymers, such as DNA helical structures. Furthermore, in addition to its application in the important physical theory of RPA, it can also be applied to the dynamic self-consistent field theory, thereby exploring the non-local dynamic response, phase transitions, rheological properties, and other phenomena in the system. In experimental settings, the structure factor represented by neural networks can be employed in the analysis of scattering experimental data, providing theoretical interpretations for the measured scattering spectra.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-023-3024-1.

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